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OVERITE AND MONTGOMERYITE: TWO NEW MINERALS FROM FAIRFIELD, UTAH

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ABSTRACT¹

Overite, $\text{Ca}_3\text{Al}_8(\text{PO}_4)_8(\text{OH})_6 \cdot 15\text{H}_2\text{O}$, is a new mineral from the variscite nodules of Fairfield, Utah. It is orthorhombic and occurs as pale green to colorless prismatic crystals, flattened on $b\{010\}$, in cavities in altered variscite. Cleavage: $\{010\}$ perfect, $\{100\}$ poor. $H=4$; $G=2.53$. Biaxial negative, $2V=75^\circ \pm 10^\circ$; $r > v$, weak; $X=c$, $Z=b$. $\alpha=1.568$, $\beta=1.574$, $\gamma=1.580$; all ± 0.002 . Elements (morphological): $a:b:c=0.7864:1:0.3795$. Structural lattice: space group $Bmam$; $a_0=14.75 \text{ \AA}$, $b_0=18.74 \text{ \AA}$, $c_0=7.12 \text{ \AA}$; $a_0:b_0:c_0=0.7871:1:0.3799$; cell contains $2[\text{Ca}_3\text{Al}_8(\text{PO}_4)_8(\text{OH})_6 \cdot 15\text{H}_2\text{O}]$.

The mineral is named after Mr. Edwin Over of Colorado Springs, Colorado.

Montgomeryite, $\text{Ca}_4\text{Al}_5(\text{PO}_4)_6(\text{OH})_5 \cdot 11\text{H}_2\text{O}$, is a new mineral from cavities in the variscite nodules of Fairfield, Utah. It is monoclinic and occurs as green to colorless lath-shaped crystals much flattened parallel to $b\{010\}$. Cleavage: $b\{010\}$ perfect, $\{100\}$ poor. Hardness 4; specific gravity 2.530 ± 0.005 . Biaxial negative, $2V=75^\circ \pm 10^\circ$; $r < v$, easily perceptible; $Z=b$, $X \wedge c = +60^\circ$. $\alpha=1.572$, $\beta=1.578$, $\gamma=1.582$; all ± 0.002 . Elements (morphological): $a:b:c=0.4145:1:0.2580$, $\beta=91^\circ 34'$. Structural lattice: space group $C2/c$; $a_0=9.99 \text{ \AA}$, $b_0=24.10 \text{ \AA}$, $\pm 0.02 \text{ \AA}$, $c_0=6.25 \text{ \AA} \pm 0.05 \text{ \AA}$; $a_0:b_0:c_0=0.414:1:0.259$, $\beta=91^\circ 28'$; $V_0=1505 \text{ cubic \AA}$; $M_0=2308$. Cell contains $2[\text{Ca}_4\text{Al}_5(\text{PO}_4)_6(\text{OH})_5 \cdot 11\text{H}_2\text{O}]$.

The name montgomeryite is proposed after Mr. Arthur Montgomery of New York City.

OVERITE

INTRODUCTION

Larsen and Shannon (1930) in their paper on the mineralogy of the phosphate nodules from Fairfield, Utah, described briefly the physical and optical properties of this mineral; lack of material at that time made further description impossible. They list the mineral as number 8 of the unnamed minerals found by them in the nodules. Although the material they worked with was not seen by this writer, the close agreement in the physical and optical properties of their mineral and the present material leaves no doubt as to their identity.

The name overite is proposed for the mineral after Mr. Edwin Over of Colorado Springs, Colorado, who, with Mr. Arthur Montgomery, recognized the mineral as new and was able to collect sufficient material for an adequate description.

¹ Abstract of overite previously published in *Am. Mineral.*, **32**, no. 12, pt. 2, p. 6 (1938). Some of the data here given is a revision of the earlier data.

OCCURRENCE AND ASSOCIATION

Overite occurs as pale green to colorless vitreous crystals in cavities in the variscite nodules. The nodules in which it is found are made up chiefly of banded intergrowths of pseudowavellite and what is believed to be deltaite, and generally have a kernel of variscite which is slightly smaller than the cavity it occupies. The overite partially surrounds and cements the variscite kernels to the surrounding pseudowavellite.

One nodule contains massive overite as irregular patches replacing variscite, pseudowavellite, and possibly deltaite. The same nodule contains small masses of a colorless mineral, *x*-ray powder picture of which is identical with apatite, but whose optical properties indicate it to be different from lewistonite, a member of the apatite group.

MORPHOLOGY

Overite is orthorhombic and nearly always occurs in well-formed crystals. There is a marked tendency toward parallel growths, although the individual crystals are easily separable. Many of the crystals measured on the goniometer gave trains of reflection in the prism zone, probably due to this tendency toward subparallelism.

The crystals are invariably flattened on {010} and are elongated parallel to the *c*-axis, although the larger crystals are sometimes platy rather than lath-shaped. One small nodule contains a few doubly terminated crystals which are attached on the front pinnacoid {100}, but in general the crystals are attached on the base. The crystals range in size from 0.3 to 4 mm. in maximum dimension. All of the crystals measured on the goniometer were small, about $0.3 \times 0.1 \times 0.05$ mm. The larger crystals all give multiple reflections from most of the faces and, therefore, generally inconsistent measurements.

Of more than 25 crystals examined on the goniometer, the measurements of twelve were used in preparing the angle table. All of the small crystals measured were taken from a single nodule; they were present as tiny single crystals in a cavity in which were many larger crystals in a crude subparallel band. The dominant forms on all the crystals are: $b\{010\}$; $q\{121\}$; and $m\{110\}$. The front pinnacoid $a\{100\}$ is always present but often very narrow. The unit prism $m\{110\}$ is small on several of the small crystals measured, but is always dominant on the larger crystals. Four prism faces $e\{150\}$, $h\{120\}$, $f\{130\}$, $k\{320\}$ can be established from their frequency of occurrence, although none are ever more than line faces, and their measured angles vary considerably. The dome $\gamma\{021\}$ was found on one large crystal as two small faces in good position and giving good reflections; it should be considered a well established form. The same crystal had two very rough and rounded faces in the position of {101} and $\bar{1}01$, but no signal was reflected

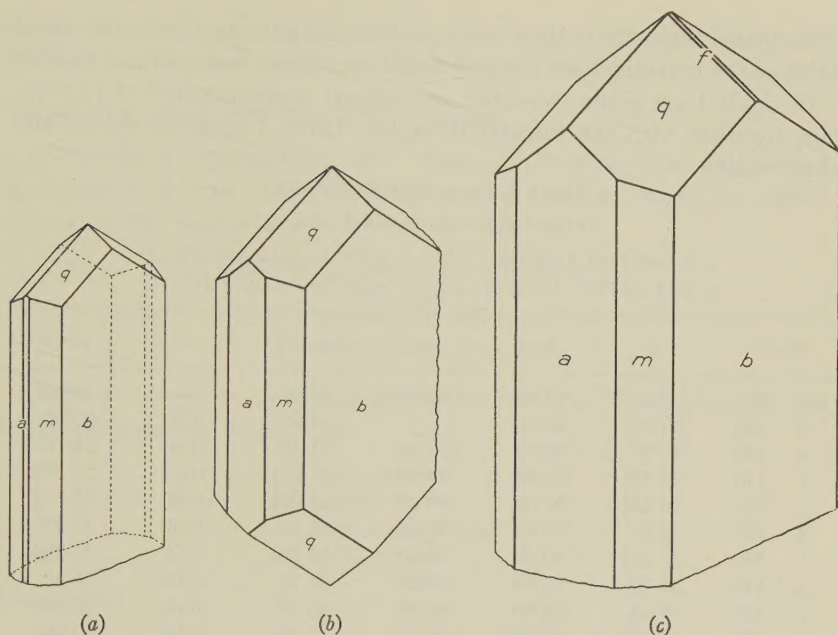


FIG. 1. Crystal drawings of overite: (a) usual habit; (b) and (c) less common habits.

TABLE 1. OVERITE—RANGE AND WEIGHTED AVERAGE OF OBSERVED ANGLES TOGETHER WITH THE CALCULATED ANGLES

Form	No. obs.	Measured Range		Best Average		Calculated	
		ϕ	ρ	ϕ	ρ	ϕ	ρ
b 010	24	—	—	0°00'	90°00'	0°00'	90°00'
a 100	21	—	—	90 00	90°00	90 00	90 00
e 150	13	12°11'–15°18'	—	14 29	90 00	14 16	90 00
f 130	5	21 58–26	—	23 19	90 00	22 58	90 00
g 250	6	26 48–29 32	—	28 16	90 00	26 58	90 00
h 120	10	29 35–33 07	—	31 53	90 00	32 27	90 00
i 350	3	37 54–38 09	—	38 03	90 00	37 21	90 00
m 110	40	51 36–53 01	—	52 10	90 00	51 49	90 00
j 430	3	59 22–60 30	—	59 50	90 00	59 28	90 00
k 320	13	61 05–63 54	—	62 23	90 00	62 20	90 00
l 310	2	74 57–75 23	—	75 10	90 00	75 19	90 00
n 410	2	78 56–78 58	—	78 57	90 00	78 53	90 00
y 021	2	–0 02 –+0 03	36°58'–372°2'	0 00	37 10	0 00	37 12
q 121	48	32 04–32 55	41 47–421°0	32 27	41 58	32 27	41 58

from them; the form is thus very doubtful. Figure 1a shows the usual habit of the crystals while Figs. 1b and 1c represent less common habits.

In Table 1 are given two-circle goniometer measurements of 12 crystals, together with the calculated angles. Table 2 presents the formal angle table.

TABLE 2. OVERITE-ANGLE TABLE
Orthorhombic dipyrarnidal—*Bmam*

$$\begin{array}{ll} a:b:c=0.7864:1:0.3795 & p_0:q_0:1=0.4826:0.3795:1 \\ q_1:r_1:1=0.7864:2.0721:1 & r_2:p_2:1=2.6350:1.2717:1 \end{array}$$

Form	ϕ	$\rho=C$	ϕ_1	$\rho_1=A$	ϕ_2	$\rho_2=B$
<i>b</i> 010	0°00'	90°00'	90°00'	90°00'	—	0°00'
<i>a</i> 100	90 00	90 00	—	0 00	0°00'	90 00
<i>e</i> 150	14 16	90 00	90 00	75 44	0 00	14 16
<i>f</i> 130	22 58½	90 00	90 00	67 01½	0 00	22 58½
<i>g</i> 250	26 57½	90 00	90 00	63 02½	0 00	26 57½
<i>h</i> 120	32 27	90 00	90 00	57 33	0 00	32 27
<i>i</i> 350	37 20½	90 00	90 00	52 39½	0 00	37 20½
<i>m</i> 110	51 49	90 00	90 00	38 11	0 00	51 49
<i>j</i> 430	59 28	90 00	90 00	30 32	0 00	59 28
<i>k</i> 320	62 20	90 00	90 00	27 40	0 00	62 20
<i>l</i> 310	75 18½	90 00	90 00	14 41½	0 00	75 18½
<i>n</i> 410	78 52½	90 00	90 00	11 07½	0 00	78 52½
<i>y</i> 021	0 00	37 12	37 12	90 00	90 00	52 48
<i>q</i> 121	32 27	41 58	37 12	68 58½	64 14½	55 38½

PHYSICAL AND OPTICAL PROPERTIES

Overite has a perfect and easy cleavage parallel to $b\{010\}$, and a poor one parallel to $\{100\}$. Most crushed fragments in a liquid under the microscope lie on this perfect cleavage, and because of the poorer cleavage are commonly elongated in the c direction with roughly parallel edges. It has a hardness near 4 (Larsen and Shannon give $3\frac{1}{2}$). Its specific gravity, determined by suspension in bromoform, is 2.53. Where it does not contain inclusions it is clear and vitreous; its color ranges from a light apple green to colorless. It is colorless under the microscope.

Optical constants:

	$n(\text{Na})$	
$X=c$	1.568	} all ± 0.002
$Y=a$	1.574	
$Z=b$	1.580	
		Biaxial negative
		$2V=75^\circ \pm 10^\circ$
		$r > v$, weak

PYROGNOSTICS

Before the blowpipe overite fuses at 2 with intumescence and leaves

a white chalky mass. In the closed tube it gives off abundant water which is neutral. It is readily soluble in hot nitric acid.

STRUCTURAL ELEMENTS AND SPACE GROUP

Weissenberg photographs were taken of the zero, first, and second layer lines with both [100] and [001] as axes of rotation, giving the following structural elements:

$$a_0 = 14.75 \text{ \AA}, b = 18.74 \text{ \AA}, c_0 = 7.12 \text{ \AA};$$

$$\text{all } \pm 0.02 \text{ \AA}.$$

$$a_0 : b_0 : c_0 = 0.7871 : 1 : 0.3799.$$

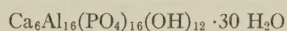
$$V_0 = 1968 \text{ cubic \AA}. M_0 = 3018.$$

Overite belongs to the space group $Bmam - D_{2h}(21)$ as given by the following observed reflections:

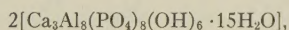
$$\begin{aligned} hkl, h+l \text{ even} \\ 0kl, l \text{ even} \\ h0l, h \text{ even}, l \text{ even} \\ hk0, h \text{ even} \end{aligned}$$

CHEMISTRY

Table 3 gives the analysis of overite, together with the molecular and atomic proportions and the atomic content of the unit cell. The analysis by F. A. Gonyer was made on a 180 mg. sample, 99 per cent pure. The cell content of overite, as derived from column 4 in the table, is



or



assuming $M_0 = 3018$ as derived from the x-ray data, and the measured gravity of 2.53. The calculated number of atoms given in column 3 are all high, indicating that the measured gravity is high. The calculated gravity for the above formula with $V_0 = 1968 \text{ cu. \AA.}$ is 2.47.

TABLE 3. ANALYSIS AND RATIOS OF OVERITE

	A	B	C	1	2	3	4
P ₂ O ₅	37.91	38.08	38.70	.268	P .536	16.18	16
Al ₂ O ₃	27.99	28.11	27.78	.276	Al .552	16.67	16
CaO	11.62	11.67	11.45	.208	Ca .208	6.28	6
H ₂ O	22.04	22.14	22.08	1.224	H 2.460	74.24	72
Insol.	0.11				O 3.606	108.83	106
	99.67	100.00	100.01				

donite. All green material labelled "gordonite" seen by the writer has proved to be the mineral described here. The present mineral is similar optically to overite, but not in other critical properties.

The name montgomeryite is proposed for this mineral after Mr. Arthur Montgomery of New York City, who, with Mr. Edwin Over, collected the material and very kindly made it available for this study.

OCCURRENCE

Montgomeryite occurs as bright green to colorless crystals in cavities in the variscite nodules. More abundantly it occurs in the nodules as massive bands in the variscite and separating the variscite kernels from the outer alterations (principally pseudowavellite) of the nodules. These massive bands frequently contain cavities into which crystals have grown. Overite has not been found associated with montgomeryite, and gordonite has been found with it in only one nodule. Englishite, one of the rarest of the minerals, very commonly occurs with it.

Montgomeryite was one of the late minerals to form, but was followed by granular coatings of pseudowavellite and a member of the apatite group which occurs as sheafs of radiating needles on montgomeryite crystals.

MORPHOLOGY

Montgomeryite is monoclinic and its crystals are always lath-shaped, flattened on {010} and elongated parallel to [001]. Wherever it occurs in open spaces it forms good crystals. Most of the crystals occur in sub-parallel growths in contact on $b\{010\}$. Only small crystals which grew free of others were suitable for measurement on the goniometer.

The crystals range in size from two millimeters to a half millimeter in longest dimension. The average dimensions of the crystals measured on the goniometer are $0.8 \times 0.5 \times 0.1$ mm. About thirty crystals were measured, of which eighteen were used in the calculations of the angle table (Table 5). Most of the crystals measured were taken from cavities in two nodules and occurred as isolated crystals attached by one end of the lath.

The habit of the crystals is very constantly lath-shaped with pyramidal terminations. The dominant form is always $b\{010\}$, generally striated parallel to [001], produced by vicinal forms in the zone [001] such that a continuous train of reflections, made up of sharp to indistinct signals less than a degree apart, is seen on the goniometer to extend as much as 40 degrees on either side of the b -face proper. In the center of the train is usually one or more very strong signals close together, one

of which can usually be established as the $\{010\}$ reflection. The vicinal faces are distributed randomly over the $\{010\}$ face, and no consistency in their angles, regardless of position or strength of signal, could be found, so that no indexing of any of these forms was possible. The pyramid $P\{\bar{1}11\}$ is always the principal terminal form; $p\{111\}$ is nearly always present, but usually small. $R\{\bar{1}31\}$ is usually present as a line face, and on a few crystals is large.

The prism forms are generally not well defined. Most of the crystals are so thin parallel to $b\{010\}$ that of necessity all prism faces are little more than lines. Added to this is the fact that most of the prism faces reflect blurred or multiple signals. The prism $m\{110\}$ is well established as the most frequent form, although it is rarely large. The form $j\{270\}$ seems well established from its frequency even though its ϕ angle is but a few degrees smaller than that of $k\{130\}$, the more reasonable form; moreover, on a very few crystals both $j\{270\}$ and $k\{130\}$ occur side by side. Other forms which seem to be established by their frequency, but

TABLE 4. MONTGOMERYITE—RANGE AND WEIGHTED AVERAGE OF OBSERVED ANGLES TOGETHER WITH THE CALCULATED ANGLES

Form	No. obs	Measured Range		Best Average		Calculated	
		ϕ	ρ	ϕ	ρ	ϕ	ρ
<i>a</i> 100	2	89°25'– 90°00'	—	90°00'	90°00'	90°00'	90°00'
<i>b</i> 010	36	—	—	0 00	90 00	0 00	90 00
190	4	14 13 – 15 52	—	15 40	90 00	15 00½	90 00
<i>f</i> 170	9	18 00 – 20 42	—	19 47	90 00	19 01	90 00
<i>g</i> 150	15	24 26 – 26 54	—	25 46	90 00	25 46	90 00
<i>h</i> 290	27	27 26 – 29 46	—	28 39	90 00	28 12	90 00
<i>i</i> 140	12	30 21 – 32 35	—	31 19	90 00	31 06	90 00
<i>j</i> 270	32	32 58 – 36 21	—	34 31	90 00	34 35	90 00
<i>k</i> 130	15	37 11 – 39 30	—	38 11	90 00	38 48½	90 00
<i>l</i> 120	2	50 20 – 50 57	—	50 20	90 00	50 20½	90 00
350	5	55 47 – 56 24	—	56 08	90 00	55 22	90 00
230	1	59 15	—	59 15	90 00	58 08	90 00
340	3	60 12 – 61 56	—	61 13	90 00	61 04½	90 00
450	2	62 55 – 64 28	—	63 42	90 00	62 37	90 00
<i>m</i> 110	35	64 47 – 70 59	—	67 33	90 00	67 29½	90 00
<i>x</i> 021	2	3 02	27°24'	3 02	27 24	3 03	27 19½
<i>y</i> 041	3	– 1 29 – +1 22	46 08 – 47°12'	0 40	46 40	1 31½	45 58
<i>p</i> 111	34	67 02 – 68 43	34 51 – 35 24	68 21	34 58	68 21	34 58
<i>P</i> $\bar{1}11$	36	– 64 52 – 67 06	32 26 – 33 35	– 66 34	32 58	– 66 33½	32 58
<i>q</i> 151	10	25 18 – 28 26	55 06 – 55 34	26 44	55 22	26 44½	55 18½
<i>R</i> $\bar{1}31$	33	– 36 04 – 38 34	43 44 – 45 50	– 37 28	44 22	– 37 33½	44 18½
<i>Q</i> $\bar{1}51$	2	– 26 36 – 29 28	53 ± – 53 14	– 26 36	53 14	– 24 46	54 51½

not by their size or constancy of angle, are: $k\{130\}$, $h\{290\}$, $f\{170\}$, $g\{150\}$, and $i\{140\}$. $l\{120\}$ was seen only twice but in one case was a large face of excellent quality and position. The front pinnacoid $a\{100\}$ was observed twice, both times a good face of moderate size. The other prism forms given without letters in the angle table can be considered very doubtful.

TABLE 5. MONTGOMERYITE-ANGLE TABLE

Monoclinic prismatic— $C2/c$ $a:b:c=0.4145:1:0.2580$; $\beta=91^\circ34'$ $p_0:q_0:1=0.6224:0.2579:1$; $\mu=88^\circ26'$ $r_2:p_2:1=3.8775:2.4133:1$ $p_0'=0.6226$, $q_0'=0.2580$; $x_0'=0.02746$

Form	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
a 100	90°00'	90°00'	0°00'	90°00'	88°26'	0°00'
b 010	0 00	90 00	—	0 00	90 00	90 00
190	15 00½	90 00	0 00	15 00½	89 35½	74 59½
f 170	19 01	90 00	0 00	19 01	89 29½	70 59
g 150	25 46	90 00	0 00	25 46	89 19	64 14
h 290	28 12	90 00	0 00	28 12	89 15½	61 48
i 140	31 06	90 00	0 00	31 06	89 11½	58 54
j 270	34 35	90 00	0 00	34 35	89 06½	55 25
k 130	38 48½	90 00	0 00	38 48½	89 01	51 11½
l 120	50 20½	90 00	0 00	50 20½	88 47½	39 39½
350	55 22	90 00	0 00	55 22	88 42½	34 38
230	58 08	90 00	0 00	58 08	88 40	31 52
340	61 04½	90 00	0 00	61 04½	88 37½	28 55½
450	62 37	90 00	0 00	62 37	88 36½	27 23
m 110	67 29½	90 00	0 00	67 29½	88 33	22 30½
x 021	3 03	27 19½	88 25½	62 43	27 17	88 36
y 041	1 31½	45 55	88 25½	44 06½	45 54	88 54½
p 111	68 21	34 58	56 58½	77 47½	33 31	57 49
P 111	—66 33½	32 58	120 45½	77 30	34 24½	119 57
q 151	26 44½	55 18½	56 59	42 45½	54 37	68 17½
R 131	—37 33½	44 18½	120 45½	56 22	45 16½	115 12½
Q 151	—24 46	54 51½	120 45½	42 03	55 31½	110 02

The pyramid $q\{151\}$ was seen on ten crystals as a very tiny face in good position, but sometimes too small to reflect a visible signal. The dome $x\{021\}$ was measured twice as a fairly large and very perfect face on one crystal and can be considered well established. $y\{041\}$ was observed as a tiny form on two crystals and on another as a fairly large face. Table 4 presents the average measured angles of each face together with the angular range and number of observations. Table 5 gives the formal angle table.

Figures 3*a* and 3*b* show the habits of the crystals; 3*a* is typical of the vast majority of the crystals; 3*b* is somewhat idealized to show $x\{021\}$ and the rare front pinnacoid $a\{100\}$. In both drawings the thickness along the b -axis is exaggerated for ease in drawing.

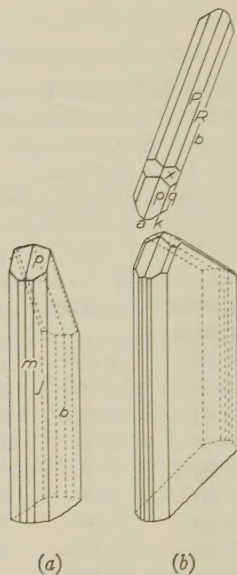


FIG. 3. Crystal drawings of montgomeryite: (a) usual habit; (b) less common forms.

PHYSICAL AND OPTICAL PROPERTIES

Montgomeryite has a perfect and easy cleavage parallel to $b\{010\}$ and a poor cleavage parallel to $a\{100\}$. This poor cleavage was observed only in immersions of the powdered mineral under the microscope.

The mineral has a hardness of 4. Its gravity is 2.530 ± 0.05 as determined on five samples, each weighing over 5 mg., on the microdensity balance. It has a vitreous luster and is usually a deep green in color, rarely pale green to colorless.

Optical constants:

	$n(\text{Na})$	Pleochroism weak	Biaxial negative
$X \wedge c = +60^\circ$	1.572	Colorless, rarely	$2V = 75^\circ \pm 10^\circ$
	1.578	pale green	$r < v$, easily perceptible
$Z = b$	1.582	colorless	
		colorless	

STRUCTURAL ELEMENTS

Rotation, and zero and first layer Weissenberg pictures about [010], and rotation, and zero layer Weissenberg pictures about [001] were taken. They gave the following values:

$$a_0 = 9.99 \text{ \AA.} \pm 0.02 \text{ \AA.}, b_0 = 24.10 \text{ \AA.} \pm 0.02 \text{ \AA.}, c_0 = 6.25 \text{ \AA.} \pm 0.05 \text{ \AA.}, \beta = 91^\circ 28'$$

$$a_0:b_0:c_0 = 0.4145:1:0.2593$$

$$V_0 = 1505 \text{ cu. \AA.} \quad M_0 = 2308 \text{ (for } G = 2.53\text{)}.$$

The space group is $C2/c - C_{2h}6$ as given by the following observed reflections:

$$\begin{aligned} hkl, h+k \text{ even} \\ h0l, h \text{ even, } l \text{ even} \\ 0k0, k \text{ even} \end{aligned}$$

CHEMISTRY

Two analyses of montgomeryite were made by F. A. Gonyer. They are given in Table 6. Analysis A was made on a 400 mg. sample, 99% pure; analysis B was made on a 230 mg. sample, 95+ % pure. Analysis A was used in the calculations.

TABLE 6. ANALYSES OF MONTGOMERYITE

	A	B	C	D	1	2	3	4
P ₂ O ₅	37.70	37.63	37.80	37.10	.265	P 530	12.24	12
Al ₂ O ₃	21.32	21.56	21.37	22.19	.209	Al 418	9.64	10
CaO	19.07	18.89	19.12	19.53	.341	Ca 341	7.87	8
H ₂ O	21.65	21.71	21.71	21.18	1.202	H 2404	55.48	54
						O 3495	80.66	80
	99.74	99.79	100.00	100.00				

A. Analysis of montgomeryite by F. A. Gonyer. Sample weighed 400 mg. and was 99% pure.

B. Analysis of montgomeryite by F. A. Gonyer. Sample weighed 230 mg. and was 95+ % pure.

C. Analysis A recalculated to 100%.

D. Theoretical composition of $\text{Ca}_4\text{Al}_5(\text{PO}_4)_6(\text{OH})_5 \cdot 11\text{H}_2\text{O}$.

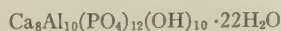
1. Molecular proportions calculated from A.

2. Atomic proportions.

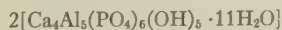
3. Number of atoms in the unit cell, assuming $M_0 = 2308$ and $d = 2.53$.

4. Theoretical number of atoms in the unit cell.

Column 4 yields the formula for the unit cell content



or



assuming $M_0 = 2308$, as given by the x-ray calculations, and the measured density of 2.53. The density calculated from this formula is 2.52.

Montgomeryite seems to have no close relation to any other known mineral. Its chemical relation to the other minerals of the phosphate nodules is shown in Fig. 2.

ACKNOWLEDGMENTS

The writer's thanks are due to Professor Charles Palache, Drs. Harry Berman and W. E. Richmond, Jr., and Mr. C. Wroe Wolfe, all of whom gave valuable assistance and advice. Mr. Arthur Montgomery spent much time and patience in sorting through his large collection of nodules for suitable material for this study.

REFERENCE

- LARSEN, ESPER S., and SHANNON, EARL V., The minerals of the phosphate nodules from near Fairfield, Utah: *Am. Mineral.*, **15**, 307-337 (1930).

STEPHANITE MORPHOLOGY

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ABSTRACT

The space-group of stephanite, Ag_5SbS_4 , left in doubt by Salvia's x -ray work (1932), is found to be $Cmc2$ by the morphological method. This result is confirmed by Weissenberg photographs.

INTRODUCTION

Stephanite has the formula Ag_5SbS_4 . It crystallizes in the orthorhombic system and is generally described as short prismatic or thick tabular in habit. This mineral affords an interesting example of the way in which Donnay's method (1938*a*) for the determination of space-groups may clear up doubtful points arising from incomplete x -ray results.

The cell dimensions and space-group of stephanite have been determined by Salvia (1932),¹ who used rotation about $[001]$ and oscillation about $[100]$ with copper radiation. He obtained the following results:

$$a_0 = 7.85 \pm 0.02, b_0 = 12.48, c_0 = 8.58 \text{ \AA}$$

$$a_0 : b_0 : c_0 = 0.629 : 1 : 0.687$$

Space-group D_{2h}^{17} (dipyramidal class) or D_2^5 (disphenoidal class), from the observed conditions, hkl present only with $(h+k)$ even, $00l$ present only with l even. Actually these conditions, if complete, admit only D_2^5 . From Salvia's tables it can be seen that there is no further condition in $0kl$ or $h k 0$; diffractions $h0l$ are not mentioned. D_{2h}^{17} requires the condition $h0l$ present only with h even and l even; this condition would admit also C_{2v}^{12} and C_{2v}^{16} (pyramidal class).

The choice left by Salvia's results is between $D_{2h}^{17}-Cmcm$, $C_{2v}^{12}-Cmc2$, $C_{2v}^{16}-C2cm$, on the one hand and $D_2^5-C222_1$, on the other hand.

In view of the wealth of crystal forms reported on stephanite, a morphological study of this species was undertaken in order to establish its space-group. Crystals from the Ungemach Collection, bequeathed to Professor J. D. H. Donnay, were placed at my disposal, together with Ungemach's own measurements. They were from the following localities: Příbram; Zacatecas and Guanajuato, Mexico; Ste-Croix aux Mines, Alsace. Crystals from the O'Brien Mine, Ontario, lent by Professor A. L. Parsons, were also studied. The goniometric measurements obtained, although largely sufficient to identify the forms and recognize twinning on (130) and (110) , were not of noteworthy quality. Goldschmidt's *Atlas* was mostly relied on for the complete form system.

The space-group, determined by the morphological method, was then checked by Weissenberg photographs.

¹ As reviewed in *Strukturbericht*, 2, 348 (1937); the original paper was not available.

MORPHOLOGICAL DATA

The one hundred and four crystal drawings of stephanite figured in Goldschmidt's *Atlas der Kristallformen* (1920), were studied in order to determine the relative form importance: (1) for each zone of the mineral and (2) for the species as a whole. The method employed is the same as that used in a previous paper, on columbite (Taylor, 1940). Some figures showing complex twinning or illegible form letters are omitted. There are one hundred and thirty-three forms listed for stephanite in the *Atlas*; a great many are doubtful. About eighty-eight forms are figured on the crystal drawings. It is clearly unnecessary to consider every form reported in a zone in order to establish the zonal character. Most of the rare or doubtful forms are disregarded in the presentation of the observation data.

In the various zones the faces can be listed as follows, in the order of observed decreasing importance (based on frequency and size):

(hkl)	$P h m r l p N$
(lkl)	$P w \gamma A (212) R$
(hkk)	$P f \zeta K \Sigma H$
$(0kl)$	$d k e t \kappa j E$
$(h0l)$	$\beta g G (102)$
$(hk0)$	$o \pi \lambda U I$

The pinakoids rank as follows: $c b a$.

GNOMONIC PROJECTION

These forms, together with all others whose indices are sufficiently small, are plotted on a gnomonic projection (Fig. 1). The forms not found on the figured crystals are also shown as points but their importance cannot be estimated and they cannot be considered as anything more than morphological curiosities.

This projection illustrates beautifully Mallard's theorem (1879), which states that the gnomonic projection is a representation of the reciprocal lattice. The main net, with a diamond mesh extending far out from the center of the projection is the first reciprocal lattice layer in true magnitude; a second net similar to the first one but on half the scale, shows the second layer; even the third and fourth layers are unmistakably evident in a third and fourth net, one-third and one-fourth of the original scale, respectively, which are restricted to the immediate vicinity of the center of projection. Note that the gnomonic poles located on the axial zones must be disregarded, inasmuch as they may be affected by glide planes; only (hkl) faces are governed by the lattice mode alone.

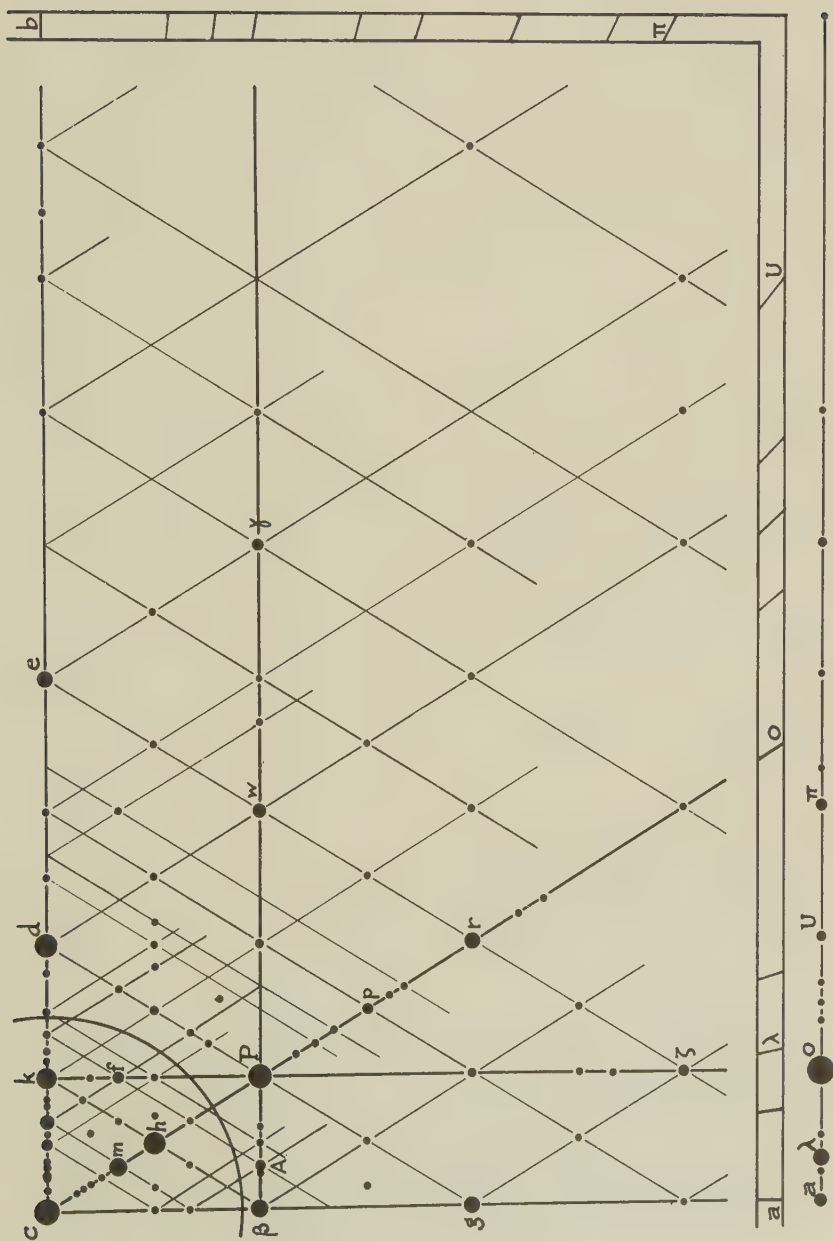


FIG. 1. Gnomonic projection of stephanite.

Figure 2 illustrates the reciprocal lattice layers from zero to five. All the observed forms which fall on each of these layers are shown by black dots. Following Peacock's nomenclature, these are the *real* nodes. The open circles represent the *virtual* nodes or those multiples of the *real* nodes which are necessary to complete the lattice net but have no morphological significance. In *x*-ray work the *real* node represents the first order of reflection actually observed; the *virtual* nodes, the other orders observed.

STUDY OF ZONAL CHARACTER

"Central" zones

Three central zones are found to have a common dominant *P*, which must therefore be noted (111).

In the zone of the (*hhl*) faces, the order *P h m r l p N* indicates a simple zone (Donnay, 1938*b*) and the indices are: *P* (111), *h* (112), *m* (113), *r* (221), *l* (223), *p* (332), and *N* (331).

The (*lkl*) faces, in the observed order of importance, are symbolized: *P* (111), *w* (131), *γ* (151), *A* (313), *-(424)*, and *R* (242). This is a double zone.

In the zone of the (*hkk*) faces, the indices must be written: *P* (111), *f* (133), *ζ* (311), *K* (155), *Σ* (422), and *H* (244). This is also a double zone.

The characters of the central zones, one simple and two double, establish the lattice as *C*-centered; the simple zone, that of the (*hhl*) faces, leading to the centered pinakoid.

"Axial" zones

In the zone of the (*0kl*) faces, the dominant is clearly *d* and the order is *d k e t κ j E*. The form *d* is (021); therefore *k* becomes (022), *e* (041), *t* (023), *κ* (043), *j* (064) and *E* (061). This zone exhibits a "shift" of the dominant, from unit position toward the *b* pinakoid, which is the normal condition for the *C* lattice.

In the zone of the (*h0l*) faces, the order is: *β g G* (102). The zone is simple, with *β* dominant and in unit position. The dominant, normally shifted away from the centered pinakoid, is here shifted back towards it by the action of a *c* glide plane; *β* must be written (202). The other forms are then indexed: *g* (402), *G* (602) and *-(204)*.

The zone of the (*hk0*) faces is double, with *o* dominant. The forms *o π λ U I* must have the indices *o* (110), *π* (130), *λ* (310), *U* (240), and *I* (150). Evidence for the zonal character follows:

π (130) is much more important than *U* (240), occurring twenty-two times in the crystals figured, against eight times for *U*; *λ* (310) is more

TABLE 2. DEVELOPMENT OF DOUBLE ZONES

Distances from pole				Zone of the (<i>h</i> <i>kl</i>) faces				Zone of the (<i>l</i> <i>kl</i>) faces				Zone of the (<i>h</i> <i>kk</i>) faces			
I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
1/7 1/5				-510 λ 310				A 313				K 155 <i>f</i> 133			
1/3	2/8	3/7													
	2/4	3/5			L 420				-424			H 244			
			4/6							φ 535					
1			6/4	<i>o</i> 110			O 460	P 111				P 111			
		5/3				11 350									
	4/2	7/3		U 240				R 242				Σ 422			
3				π 130				<i>w</i> 131				ζ 311			
	8/2	11/3		I 150	-280			γ 151							
5					-2.12.0										
7	12/2			<i>l</i> 70											
9				-190											
11				<i>i</i> 1.11.0											
13				1.13.0											
15				-1.15.0											
Also reported in <i>Atlas</i> :				C 161=2.12.2 Artini (1891); Nejd (1895). -727=14.4.14 Vrba (1886). M 818=16.2.16 Artini (1891); Nejd (1895).				-522=10.4.4 Nejd (1895). -833=16.6.6 Slavik (1901-2). Σ 13.4.4=26.8.8 Artini (1891); Nejd (1895). Σ 18.5.5=36.10.10 Artini (1891); Nejd (1895).							
-340=680 Slavik (1901-2) -3.10.0=6.20.0 Slavik (1901-2); also in Ungemach's notebooks (twice).															

important than L (420), occurring on eleven figures whereas L is found only once. This zone abides by the normal condition for a C lattice.

Lists of tautozonal faces were prepared (Tables 1 and 2) to illustrate the morphological development of the central and axial zones of stephanite. These tables should be compared with those given by Donnay (1938*b*), in which the theoretical development of various types of zones is demonstrated. Table 1 deals with the simple zones. The first column shows the distances² from the gnomonic pole, while each subsequent column gives the corresponding forms in the zone considered. Forms anomalously absent have their symbols italicized. Table 2 presents similar data for the double zones.

Such tables are illuminating. They show, for instance, that, in the zone of the ($hk0$) faces, if we consider the section between o (110) and π (130), U (120) must become (240) because of the presence of u (350), which is in turn justified by the presence of (460). This eliminates any doubt as to the character of the zone. Attempting to make it a simple zone, one could account for (230) as a secondary face, between (110) and (120), the tertiary faces becoming (340) and (350). This scheme is open to the following objections: U (120) is made more important than π (130); (230), more important than (350); and there should be a face (340) more frequent than (350), all of which is contrary to observed facts.

Similarly the decision that k must be written (022) is borne out by the presence of the secondary face κ (043), and the tertiary faces j (064) and ι (065). If k were to be considered as (011), the face j would become (032), more important than k (043), and ι (065) could only be accounted for by inserting a face (054), which has not been reported. Again, s would become (012), hence more important than t (023); and the face (034), unreported, would be required to explain the presence of (035) and (045).

Pinakoids

The axial zones, being so well established, determine the character of the pinakoids. That is, a and b must be doubled because they terminate a double zone; they are therefore written (200) and (020). Also it is necessary that c be doubled and become (002) on account of the "shift" of the dominant β , in the zone of the ($h0l$) faces, toward c . There is an anomaly to be reported in this respect: the theoretical order (bca) conflicts with the observed order (cba). The zonal data are quite reliable and outweigh the observations on the order of the pinakoids.

² These distances are interrelated by Peacock's Harmonic-Arithmetic Rule (1937).

MORPHOLOGICAL DETERMINATION OF THE SPACE-GROUP

Two stereographic projections are given (Figs. 3a and 3b). In these projections only the dominant form in each zone is shown. The characters of the zones and dominants are indicated: a single line represents a simple zone and a double line, a double zone; a black dot represents a form with coprime indices and an open circle, a form with doubled indices. Figure 3a represents the "initial pattern" (Donnay, 1939) of the C lattice, while Fig. 3b gives the pattern observed for stephanite.

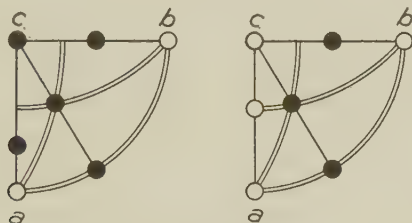


FIG. 3a. Aspect C^{***} . Fig. 3b. Aspect C^*c^* .

It is seen in the first of these that the criteria for the "initial pattern," or the aspect C^{***} are as follows: One of the central zones, that leading to the c face, is simple while the other two are double; the two axial zones that intersect in the centered pinakoid exhibit a "shift" away from unit position toward the b and a pinakoids, respectively; the zone of the $(hk0)$ faces is double and the indices of the a and b faces are doubled. In the second projection the aspect represented is C^*c^* ; the only changes indicating a c glide plane lie in the "shift" of the dominant in the zone of the $(h0l)$ faces and the doubling of the indices for all the faces in the zone (including c).

The characters of the "central" zones show that the lattice is C . In the discussion of axial zones it is shown that the zone of the $(0kl)$ faces obeys the C criterion. In the zone of the $(h0l)$ faces, the "shift" of the dominant indicates the (010) plane to be a c glide plane. The third zone, that of the $(hk0)$ faces, is again normal for the C lattice.³ Therefore the morphological aspect is written C^*c^* and the symmetry class 222 is ruled out.

This aspect admits of three possible space-groups: $Cmcm$, in the holohedry $(2/m\ 2/m\ 2/m)$, and $C2cm$ or $Cmc2$, in the antihemihedry $(2mm$ or $mm2)$. The frequently noted twinning on (001) , established by Miers (1889), is incompatible with the holohedry, since (001) cannot be a plane

³ The fact that only one axial zone violates the condition imposed by the C lattice accounts for the correct determination of the lattice made by Friedel (1904), on the strength of the classical Law of Bravais alone.

of symmetry. The fact that, in the present setting, the c -axis is a two-fold axis eliminates the possibility of $2mm$ in the antihemihedry. Hence the class must be $mm2$ and the space-group is uniquely determined as $C_{2v}^{12}-Cmc2$.

X-RAY DETERMINATION OF THE SPACE-GROUP

Since the space-group of stephanite, as determined by its morphology, was compatible with Salvia's work, provided $h0l$ diffractions be present only with h and l even, it was thought desirable to check the space-group by means of Weissenberg photographs, with special attention to the diffractions $h0l$. This was done in the Department of Mineralogy, University of Toronto, with the assistance of Professor M. A. Peacock and Mr. L. G. Berry using a small twinned crystal from Ste-Croix aux Mines, Alsace (Ungemach Collection).

The following photographs were taken with copper radiation: rotation about $[001]$ and Weissenberg photographs of the zero, first, and second layer lines. In view of the complication of the pattern due to twinning on (110) , and some random spots from adhering foreign material, reciprocal lattice nets were constructed to ensure correct indexing. The following results were obtained:

$$a_0 = 7.70, b_0 = 12.32, c_0 = 8.48, \text{ all } \pm 0.05 \text{ \AA}$$

$$a_0:b_0:c_0 = 0.625:1:0.688$$

in fair agreement with Salvia. The morphological ratios for the Ste-Croix crystal (calculated from Ungemach's one-circle measurements) are:

$$a:b:c = 0.6285:1:0.6856.$$

For the material from the O'Brien mine, my two-circle measurements yielded:

$$a:b:c = 0.6289:1:0.6847.$$

Dana gives the following values:

$$a:b:c = 0.6291:1:0.6851.$$

TABLE 3. DIFFRACTION SPOTS OBSERVED ON THE
WEISSENBERG PHOTOGRAPHS

	Zero-layer	First-layer	Second-layer
hkl		$(h+k)$ even	$(h+k)$ even
$0kl$		021, 041, 061, 081, 0.10.1, 0.12.1, 0.14.1	022, 042, 062, 082, 0.10.2, 0.12.2, 0.14.2
$h0l$		All absent	202, 402, 602, 802
$hk0$	$(h+k)$ even		
$h00$	200, 400, 600		
$0k0$	020, 040, 060, 080, 0.10.0, 0.14.0		
$00l$		Absent	002

Table 3 lists the diffraction spots observed in the different zones. The observed diffractions conform to the condition, hkl present only with $(h+k)$ even. No further condition is observed, except in the critical zone of the $h0l$ planes,⁴ where all $h01$ are absent, all $h02$ with h odd are also missing, while all $h02$ within reach are present with h even.

If one relies on *absence* of diffraction spots, the aspect C^*c^* may be considered confirmed. If, on the other hand, one demands *presence* of diffraction spots to bolster his conclusion, then the space-group $C222_1$ will still remain a possibility from the x -ray standpoint. The morphological method is here at an advantage, for the fact that the zone of the $(h0l)$ faces is a simple zone, with β (202) dominant, firmly establishes the extinction criterion and the concomitant c glide plane.

The holohedral class being ruled out by the twinning data and the c axis being a symmetry axis, the space-group $Cmc2$, determined by morphology, is thus confirmed within the limitations of the x -ray method.

ACKNOWLEDGMENTS

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It is also a pleasure to record my indebtedness to Professor M. A. Peacock, University of Toronto, who kindly put at my disposal all the facilities of his laboratory and who, with Mr. L. G. Berry, assisted and instructed me in the technique of taking Weissenberg pictures.

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⁴ The previous uncertainty in the zone $h0l$ may be connected with the complication caused by twinning, which is common in stephanite. On the film (hkl) a spot was noted near the position 401 for the principal individual. On careful measurement it was decided that this spot was definitely displaced beyond the limit of error in measuring on the photograph. If 401 were present, then of course the condition $h0l$ with h even and l even would not exist.

CRYSTAL HABIT VARIATION IN SODIUM FLUORIDE*

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ABSTRACT

The effect of 143 inorganic and organic cosolutes, other than dyes, on the crystal habit of NaF was investigated experimentally. The cosolutes which effect variation from the ordinary cubical habit of NaF fall into two groups:

(1) Cosolutes which contribute OH⁻ ion to the solution cause a change in habit to octahedral. With increasing cosolute (OH⁻) concentration, the NaF progressively crystallizes as cubes, skeletal cubes, skeletal octahedra and, above a liminal value, as octahedra. At still higher concentrations, a habit reversal, from octahedral back to cubic, may be observed.

The habit change is due to the substitutional adsorption of OH⁻ for F⁻ in the surface of the growing NaF crystals. The mechanism correlates with that found by Buckley for crystals of MRO_x and foreign ions of the type RO_x. The process by which the adsorption effects the change in habit finds explanation in terms of the growth mechanism demonstrated by Kossel and by Stranski for ionic crystals of the NaCl-type.

(2) Cosolutes which react to form double-salts with NaF. The habit variation is related to structural coincidences between crystals of NaF and of the double-salt, and marks an

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approach to a double-salt phase boundary in the solute-cosolute system. The adsorption is not by substitution, but involves the formation of a two-dimensional, essentially crystalline, double-salt phase in ordered apposition to the surface ions of the NaF crystals. The arrangement and spacing of the units composing the adsorbed layer of double-salt is so effected, by choice of adsorbing plane in the NaF, to be that proper to crystals of the double-salt itself. The habit variation in the NaF is a concomitant of this choice of adsorbing plane. The general situation correlates with the theory of double-salt formation advanced by Seifert and with the point of view of habit variation taken by Bunn.

The essential continuity of the crystal-adsorption mechanisms of Buckley and of Bunn is pointed out.

INTRODUCTION

It is a familiar fact that the habit of a crystal may be made to vary by the addition of a cosolute to the crystallizing solution. In recent years investigations directed at the cause of this effect have been largely concerned with the interpretation of crystal-adsorption in terms of crystal chemistry. In this direction, the researches of Buckley (1) have led to the recognition of similarities in size and shape between single ions of the cosolute and of the growing crystal as factors in the adsorption. On the other hand, Bunn (2) and later Royer (3) and Frondel (4) have emphasized the importance of coincidences in structure between the growing crystal and crystals of the cosolute in influencing the adsorption.

An essential difference is found between these views. According to Bunn, the adsorbed material is an essentially crystalline, continuous, two-dimensional phase which plates the surface of the adsorbing crystal much in the manner of an oriented overgrowth. The kind and degree of structural coincidence between the growing crystal and the adsorbed crystal-phase, and the habit of the latter, determines both the occurrence of adsorption and the direction of habit change. Buckley, on the contrary, views the adsorbed units as being scattered over the adsorbing surface, independent of each other and without the mutual interaction necessary to define crystallinity between themselves. The occurrence of adsorption and the choice of adsorbing plane in this view involves only geometrical considerations between the types of single ions involved.

OBJECTIVES OF THE INVESTIGATION

The present study was undertaken in hope of evaluating in the alkali halides the adsorption controls advanced by Buckley and by Bunn. The influence of inorganic and organic cosolutes, other than dyes, on the crystal habit of NaF and some related halides is described in this paper. Approximately 600 separate crystallizations were made, with 143 different cosolutes. The influence of 112 dyes on the habit and optics of NaF, LiF, NaCl, KCl, KBr and KI have been described in a previous paper (8).

Most of the recent work in the field has been concerned with substances, mostly salts of oxy-acids, that are relatively complex in structure and motif-configuration. The alkali halides of the NaCl-type seem specially suited for investigation, by reason of their simplicity of structure and motif, the detail in which their crystal chemistry is known, and the wealth of older experimental observations on their habit. Most important, the mechanism of growth from pure solution of the ionic NaCl-type crystals has been semi-quantitatively analyzed, by Kossel (5) and by Stranski (6), and is in agreement with observation (7).

EXPERIMENTAL TECHNIQUE

The crystallizations were made from 200 cc. volume by partial evaporation at 80°C. in an electric oven. This temperature was selected to permit parallel experiments on other alkali halides, some of which crystallize as hydrates at lower temperatures. The time of crystallization was usually 40 to 60 hours. Glass wool was added to the solutions, in the absence of free HF or strong alkali, to permit free development of the crystals. Beakers coated with alkali- or acid-resistant resin were used when necessary.

TYPES OF HABIT VARIATION IN NaF

CRYSTAL HABIT OF NaF FROM PURE WATER SOLUTION

NaF crystallizes as cubes from pure water solution at temperatures from 22° to *ca.* 100°C. and under conditions of either fast or slow growth. The other halides of the NaCl-type (Table 1) also crystallize from pure water as cubes. The habit from water is unknown for LiBr, LiI and β -CsCl and uncertain for CsF.

TABLE 1. ALKALI HALIDES OF THE NaCl-TYPE

a_0	a_0	a_0	a_0	a_0
LiF 4.020	NaF 4.619	KF 5.333	RbF 5.63	CsF 6.008
LiCl 5.14	NaCl 5.628	KCl 6.278	RbCl 5.54	β -CsCl 7.10
LiBr 5.490	NaBr 5.962	KBr 6.578	RbBr 6.854	
LiI 6.000	NaI 6.462	KI 7.052	RbI 7.325	

The reason for the assumption of a cubical habit by these substances has been demonstrated by Kossel and by Stranski. Analysis of the energy changes accompanying the removal from solution, dehydration and ordered packing of alkali halide ions into a NaCl-type structure shows that the most stable configuration of surface ions is that of {100} planes. The ability to resolve accretion, or growth rate, of the {100} planes is hence a minimum, and the crystals develop as cubes.

It should be emphasized that the choice of surface configuration of ions, or habit, necessarily is an expression of the same factors that fix the choice of internal configuration of ions, or structure-type. These factors include the size, charge, hydration and polarizability of the ions concerned and, in addition, what may be termed environmental factors, namely, temperature, pressure, and the presence of foreign ions. Thus hydrostatic pressure may effect variation in structure-type, as with RbCl (9), and may also effect variation in crystal habit (10). The influence of temperature and of foreign ions on both choice of structure-type and of habit is a commonplace of genetic crystallography. Habit is the surface response of a crystal structure, or phase, to environmental conditions varying within the limits of stability of the phase itself.

CRYSTAL HABIT OF NaF FROM SOLUTIONS CONTAINING COSOLUTES

Variation from the ordinary cubic habit of NaF is found to accompany the presence of particular kinds of cosolutes in the crystallizing solution. The habit-varying cosolutes can be separated into two broad groups:

(1) Cosolutes which contribute OH^- ion to the solution, when present above a liminal concentration, change the habit of NaF to octahedral. The experimental observations which characterize this type of habit variation, and the mechanism by which the adsorption effects the change in habit, are described in Part I of this paper.

(2) Cosolutes which react to form double-salts with NaF . The experimental observations which characterize this type of habit variation, and the mechanism by which the adsorption effects the change in habit, are described in Part II.

PART I. EFFECT OF HYDROXYL ION ON THE HABIT OF NaF

SUMMARY OF EXPERIMENTAL OBSERVATIONS

The experimental observations which relate to the effect of hydroxyl ion on the habit of NaF may be summarized as follows:

1. The habit of NaF is changed to octahedral by all cosolutes which afford OH^- ion. The OH^- may be contributed directly, as by NaOH and other bases, or by hydrolysis, as with Na_2CO_3 and other salts of strong bases and weak acids. The data from which this conclusion is drawn are listed in Tables 2 and 3.

2. The habit-varying property of the OH^- -affording cosolutes is lost if the solution is made acid. Neutral cosolutes (NaCl , glycerin, etc.), cosolutes acid by hydrolysis ($(\text{NH}_4)_2(\text{SO}_4)$) and acids do not cause habit variation. Some specific exceptions to the latter statement are described in Part II.

3. A certain cosolute (or OH^-) concentration, which differs for different cosolutes, is necessary before octahedra are formed. In general, as the OH^- concentration is increased from zero, the outward form of the NaF progressively changes from perfect cubes through

skeletonized cubes, skeletonized octahedra and, finally, above the liminal OH^- concentration, to perfect octahedra. With Na_2CO_3 a progressive habit reversal, from octahedral through cubo-octahedral back to cubic, may occur if the concentration is increased still further. This sequence does not refer to changes in a given crystallization, but to successive experiments carried out at stepped cosolute concentrations. The experimental data for a particular cosolute, Na_2CO_3 are cited in Table 3, and the corresponding growth forms are represented in Figs. 1 to 9.

The concentration of a few OH-affording cosolutes, including very weakly alkaline substances and cosolutes which react to prohibit the crystallization of NaF, cannot be built sufficiently high to cause the formation of anything other than skeletal growths.

4. The habit-varying effect of OH ion is peculiar to the alkali fluorides: NaF, LiF and KF. RbF and CsF were not investigated. Neither octahedra nor skeletal growths are produced by OH^- with the alkali chlorides, bromides or iodides. The experimental data for these substances is given in Table 4.

TABLE 2. INEFFECTIVE COSOLUTES, AND EFFECTIVE
COSOLUTES OF THE HYDROXYL-TYPE

*Cosolute concentration given in mols per mol NaF, unless
otherwise stated.*

INEFFECTIVE COSOLUTES

Halides. NaCl 1.0, 0.02. NaI 0.35, 0.02. NaBr 0.4, 0.02. NH_4F 1.0, 0.02. NH_4Cl 4.7, 1.0, 0.02. NH_4Br 1.0, 0.02. NH_4I 1.0, 0.02. LiF sat'd soln. KF 3.0, 0.02. KCl 1.0, 0.02. KBr 0.2, 0.10, 0.02. KI 0.2, 0.02. SnCl_2 (acid) 0.05. Also saturated with the following substances (the solubilities are very small): CdF_2 , CoF_2 , CuF_2 , CaF_2 , FeF_3 , PbF_2 , SbF_3 , ZnF_2 , ThF_4 , CeF_4 and LaF_4 .

Salts of inorganic acids. NaClO_3 0.4, 0.2, 0.05. $\text{Na}_2\text{Cr}_2\text{O}_7$ 0.15, 0.05. Na_2CrO_4 0.15, 0.06, 0.02. NaIO_3 0.125. Na_2MoO_4 0.17, 0.08, 0.01. NaNO_3 0.8, 0.06. NaNO_2 0.6. $\text{Na}_2\text{S}_2\text{O}_3$ 0.1. $\text{Na}_2\text{S}_2\text{O}_6$ 0.2, 0.04. NH_4NO_3 0.5. $(\text{NH}_4)_2\text{CrO}_4$ 0.27. $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ 0.52. KClO_3 0.25. KClO_4 sat'd soln. K_2CrO_4 0.2, 0.06. KIO_3 0.19, 0.09. $\text{K}_2\text{Cr}_2\text{O}_7$ 0.15, 0.05. KMnO_4 1.25, 0.1. KNO_3 0.6, 0.05. TiSO_4 0.1.

Salts of organic acids. Na acetate 0.2, 0.05, 0.01. Na oleate 0.01% soln. Na oxalate 0.24. Na salicylate 0.25. NaCNS 0.5. NH_4 acetate 0.52, 0.05. NH_4 citrate 0.1, 0.015. NH_4 oxalate 0.18, 0.06. NH_4H oxalate 0.04. NH_4 tartrate 0.22. K acetate 0.4, 0.2, 0.05. K oxalate 0.22, 0.05. $\text{K}_4\text{Fe}(\text{CN})_6$ 0.1. $\text{K}_3\text{Fe}(\text{CN})_6$ 0.1. KH phthalate 0.2, 0.05. KH oxalate 0.3, 0.04. KH tartrate 0.21.

Organic substances. Acetamide 1.0. Asparagine 0.04. Carbamide (urea) 6.0, 3.3, 1.0; also ineffective at 6.0 at 23°C . Dextrose 0.3. Diethylene glycol 2.0. Formamide 1.5, 0.75. Gelatin 1% soln. Glycerine 2.7. Glycocoll 1.0. Gum arabic 4% soln. Pectin 0.5% sol. Resorcinol 0.05. Starch 0.5% soln. Succinamide 0.5. Sucrose 0.3. Terpin hydrate 0.05. Thiocarbamide 1.0. Quinine sulphate sat'd soln.

Acids (concentrations in normalities). Acetic 0.3. Benzoic 0.25. Carboic 0.43 (at 23°). Citric 0.3, 0.07. Formic 3.0 (at 23°). HCl 0.3, 0.05. HNO_3 0.3, 0.05. H_2SO_4 0.3, 0.08, 0.01. H_3PO_4 0.42, 0.15, 0.05. Lactic 2.0 (at 23°). Oxalic 0.1, 0.01. Picric 0.005. Propionic 2.0 (at 23°). Salicylic 0.08. Tannic 0.5% soln. Tartaric 0.1, 0.01.

EFFECTIVE COSOLUTES. SEE ALSO TABLE 6.

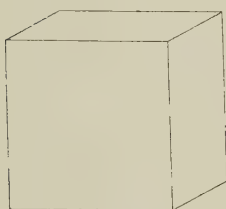
 o = octahedra a = cubes

NaOH: o at 0.3, 0.1, 0.05, 0.025; a at 0.0025, 0.001. KOH: o at 0.7, 0.25, 0.09; a at 0.045, 0.017, 0.009. Na_2CO_3 (see Table 3). K_2CO_3 : o at 0.46, 0.072; a at 0.0009. NaHCO_3 : o at 0.5, 0.06; a at 0.001. KHCO_3 : o at 0.4; a with small o faces at 0.05; a at 0.001. $\text{Na}_2\text{B}_4\text{O}_7$: o with small a faces at sat'n.; a at 0.125, 0.06, 0.02. NaCN: o at 1.0, 0.05. KCN: o at 1.0. Na_2SO_3 : o at 0.32. Na_2WO_4 : o at 0.15, a with small o faces at 0.06. K_2WO_4 : a with small o faces at 0.1, a at 0.055. Sodium citrate: o with small a faces at 0.15, 0.075, 0.0037, 0.0015; a at 0.0001. Sodium tartrate: o with small a faces at 0.5; a at 0.2. Potassium tartrate: cubo-octahedra at 0.5; a with small o faces at 0.2, a at 0.07. NaK tartrate: a with small o faces at 0.15; a at 0.05.

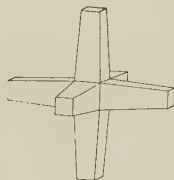
TABLE 3. VARIATION IN OUTWARD FORM OF NaF WITH OH^-
(Na_2CO_3) CONTENT OF THE SOLUTION

Initial concentration of Na_2CO_3 in g./100 cc. NaF solution. ^a	Outward Form of NaF crystals
0	Cubes. Fig. 1
<0.001	Imperfect, composite, cubes; parallel aggregates of cubes.
>0.005 <0.03	Skeletal cubes. Figs. 2 and 3.
>0.05 <0.1	Skeletal octahedra, grading to composite octahedra. Figs. 4 and 5.
>0.2 <1	Octahedra. Fig. 6.
>2 <8	Octahedra modified by (100); (100) increasing in size with concentration. Figs. 7 and 8.
>10 to 30	Cubes. Fig. 9.

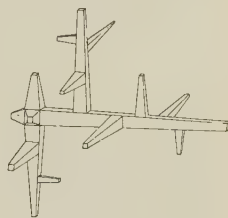
^a Summarized from 76 separate crystallizations at stepped concentration intervals. Check runs over portions of the sequence agreed internally, but did not correlate exactly with other sequences.



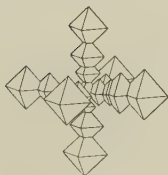
1.



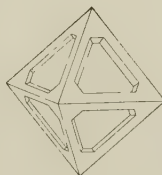
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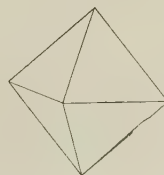
3.



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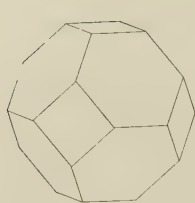


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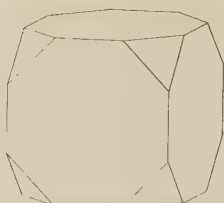


6.

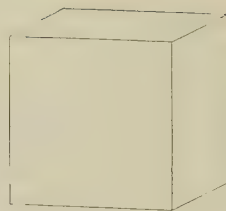
FIGS. 1-6. Sequential habit variation in NaF.



7.



8.



9.

FIGS. 7-9. Sequential habit variation in NaF.

TABLE 4. EFFECT OF OH ON THE HABIT OF SOME NaCl-TYPE ALKALI HALIDES

Cosolute concentrations cited are in mols per mol AB or in mols per liter; other data from literature. Crystallized at 80° for new data, and at ca. 24° for literature.

The pure solution habit of these halides is cubic.

	NaOH	KOH	Na ₂ CO ₃	K ₂ CO ₃	NaCN	KCN
LiF	111 (Table 5)					
NaF	111 (See Tables 2 and 3)	111	111	111	111	111
NaCl	100 ^a 0.1, 0.25 M/M	100	100 0.2 M/M	100		
NaBr	100 0.1, 1.0 M/M				100 3 M/L	
NaI	100 0.1 M/M					
KF		111 ^b 0.1, 10 M/L				
KCl	100 0.2 M/M	100 0.1, ~sat'd	100 0.1, sat'd	100 ^d		100 4 M/L
KBr	100 0.05 M/M	100 ^c	100	100		100 4 M/L at 40°
KI	100 0.05 M/M	100				100 5 M/L at 40°

^a 10% NaOH is said to give tiny modifying {111} faces, and 20% NaOH slightly larger {111} faces. "Strong" NaOH is said to give cubes in fast growth and cubo-octahedra in slow growth. NH₄OH gives cubes.

^b At 40°C. A birefringent hydrate (?) was obtained at lower temperatures. KF crystallizes with difficulty.

^c KOH is variously said to give cubes or cubo-octahedra.

^d K₂CO₃ is variously said to give cubes or octahedra.

MECHANISM OF THE HABIT VARIATION

Substitutional Adsorption of Hydroxyl Ion. In the foregoing discussion the habit-varying property possessed by a number of cosolutes for the alkali fluorides was identified as OH ion. As is seen from the accompanying list, the ionic radius of OH⁻ is nearly identical with that of F⁻ and is considerably smaller than that of Cl⁻, Br⁻, or I⁻.

	OH ⁻	F ⁻	Cl ⁻	Br ⁻	I ⁻
Ionic radius (for C.N.6):	1.35	1.33	1.81	1.96	2.19

This suggests that during the growth of the fluoride crystal an OH ion can slip into a position intended for an F ion. Isomorphous substitution between these ions is, in fact, found in many minerals.

NaF crystals grown from solutions containing OH⁻ and F⁻ in the ratio of 1:2 were found analytically¹ to contain only 0.003 per cent OH, corresponding to 1 substituted OH ion for about 13,500 F ions. This amount of OH⁻ seems entirely too small to be alone responsible for the habit variation, although no evidence can be brought to justify this view. Admitting the essential role of OH⁻, the habit variation may also be ascribed to OH ions which substitute for surface F ions of the growing NaF crystals and, after a brief life span (adsorption) on the surface, are displaced by F ions through competition from the solution.

The consequences in point of habit variation of a substitution of OH⁻ for F⁻, either transient or permanent, may now be considered. As shown by Kossel and by Stranski, the growth of {100} planes in an ionic NaCl-type crystal takes place essentially *per saltum*, by the deposition of successive ion layers. Accreting ions or ion-pairs are not attached with equal ease to the various positions of surface coordination in the {100} planes, but deposit most readily at corner positions, less readily at edges, and least readily in face interior positions. An ion-layer once initiated tends to complete itself, by spreading laterally row by row over the surface, before the deposition of a new layer, since less energy is required to continue the growth of an already initiated layer than to start a new layer. This mechanism emphasizes the effect of substitution, in that a few foreign ions, strategically placed at the corners or at the ends of incomplete rows, may block the spreading of an entire layer. The idea is implicit that the foreign ion is unable to fill the role in the growth process proper to the ion species for which it substitutes.

¹ The OH content was estimated by comparing the *pH* of a solution of NaF crystals previously re-crystallized from pure water with that of crystals grown slowly (60 hours) from a solution containing added NaOH. The crystals were repeatedly washed in saturated NaF solution made acid with HF, and in water. The *x*-ray powder patterns of the two preparations were identical in spacing and intensities.

Substitutional blocking of the nature described, involving an equal ease of substitution of the foreign ion at all surface positions, would only result in a general slowing of growth of the crystal without habit variation. It is well known, however, that there are relative differences in the ease of attachment of foreign ions and of crystal ions to the various surface positions. The edges and corners of crystals are found to play a special role in this regard, and serve as active spots in crystal adsorption.² The development of skeletal growths and of octahedra in NaF is believed primarily due to the preferential deadening of the cube-corner centers of nucleation by the substitution of OH ions therein. This places greater emphasis in the growth process on nucleation from face-interior positions, which, while inherently less favorable during pure growth, are now relatively more free from foreign ions. The lateral spreading of ion-layers thus initiated, however, generates new corner positions, which may then be selectively occupied and deadened by additional foreign ions.

Octahedra as a Consequence of Ion Substitution. The essential circumstance for the development of octahedra is the incomplete overlap at the cube-corners of successive ion-layers. The geometry of the situation is such that the successive coplanar set-backs thus generated define an octahedron. In terms of Haiüy's derivation of secondary forms, the regular periodicity in the deposition of successive non-overlapping layers of "molecules integrantes" defines a (coplanar) surface with rational indices.

The above situation can hold only above a limiting incidence of OH⁻, to be identified with the experimentally observed liminal OH⁻ concentration, at which the corner positions are occupied and deadened as soon as they are generated. At lesser rates of substitution of OH⁻ (low cosolute concentrations) one or more exactly superposed ion-layers may be deposited, as in growth from pure solution, before the growth is interrupted by the substitution of an OH ion into a corner position. This mechanism presumably applies to the formation of the skeletal crystals observed below the liminal concentration of OH⁻. No simple geometrical explanation of the process is apparent.³

² The substitutional adsorption of ThB for Pb in the edges and corners of growing PbCrO₄ crystals, demonstrated by Schwab, G. M. and Pietsch, E. (*Zeits. phys. Chem.*, **2B**, 262, 1929) is an instance in point. The frequent localization of a super-crystallizing mineral to the edges and corners of the incrustated crystals is a further illustration (Fron del, C.: *Am. Mus. Nat. Hist. Novit.*, **759**, 1-15, 1934).

³ The development of skeletons is peculiar to OH⁻ in low concentrations. Ordinary cubes are obtained from pure solution in either slow or fast growth, from solutions containing gum arabic, gelatine, starch and other thickening agents, and from solutions containing acids and other non-alkaline ineffective cosolutes.

Habit Reversal at High Cosolute Concentrations. Na_2CO_3 has a peculiar effect, not hitherto noted in habit variation studies, on the habit of NaF . If the concentration of Na_2CO_3 is increased considerably above that necessary to produce octahedra, modifying cube faces appear on the octahedra and gradually increase in size with concentration (in separate crystallizations) until finally only simple cubes are formed. The experimental data are tabulated in Table 3, and the habits shown in Figs. 7, 8 and 9. Habit reversal was not observed with Na_2SO_4 , Na_3PO_4 or H_3BO_3 . Other cosolutes were not systematically investigated in this regard.

LiF was also found to exhibit habit reversal, in the presence of NaOH . The data are listed in Table 5. The liminal concentration of OH^- necessary to produce octahedra in LiF is much greater than with NaF .

TABLE 5. VARIATION IN OUTWARD FORM OF LiF WITH OH^- (NaOH) CONTENT OF THE SOLUTION

Final conc. of NaOH in g./100 cc. LiF solution ^a	Outward Form of LiF crystals
<1	Mixtures of cubes and skeletal cubes.
>5 <15	Mixture of warty cubic crystals and aggregates with ordinary cubes and skeletal cubes. Some crystals with octahedral faces at higher concentrations.
>20 <80	Mostly cubo-octahedra mixed with octahedra; some cubes and warty growths.
>100	Cubes.

^a Summarized from 18 separate crystallizations.

The variation from octahedral back to cubical appears to be the final consequence of the substitutional-adsorption mechanism previously outlined. Cube faces make their first appearance on the octahedra when the concentration of OH^- becomes sufficiently high to interfere with nucleation from the face-interior positions. The preferential substitution of OH^- at the corners, which is responsible in the first place for the formation of octahedra, is then relatively less important, and OH^- and F^- compete on a more equal basis for all positions of surface nucleation. This is equivalent to the situation in pure growth, and a cubical habit develops.

PART II. EFFECT OF DOUBLE-SALTS ON THE HABIT OF NaF

SUMMARY OF EXPERIMENTAL OBSERVATIONS

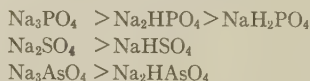
A group of cosolutes can be recognized which effect habit variation in NaF by a mechanism different from that of the OH-affording cosolutes described in Part I. These cosolutes comprise the normal and, to a less extent, the acid, alkali sulphates, phosphates, arsenates and vanadates, and probably also H_3BO_3 and Na_2BrO_3 . The experimental data relating to these substances are summarized in Table 6. The distinctiveness of the group is indicated by the following considerations.

1. Hydroxyl ion is not the habit-varying agent, since the cosolutes remain effective if the crystallizing solution is made faintly acid.

2. Substitution of the cosolute anions in place of single ions in the NaF structure, analogous to the substitution of OH^- for F^- , appears impossible because of marked differences in the size, shape and charge of the ion-species involved. Dimensional coincidences are also lacking for the attachment of the (tetrahedral) cosolute anions to the crystal by the substitution of a face or edge of the tetrahedron for groups of adjoining F ions in the NaF. While a triangular configuration of F ions is found in $\{111\}$ planes of the halide, the inter-ionic distances are considerably greater than the triangle sides of the cosolute tetrahedra. The values for the halides increase in the series $\text{Li}^+ \rightarrow \text{Rb}^+$ and $\text{F}^- \rightarrow \text{I}^-$ from 3.26 Å in NaF to 5.18 in RbI. These values compare with a triangle side, or O—O distance, of *ca.* 2.8 in the RO_4 ions.

3. The habit variation is independent of the cosolute ions as individuals, but instead appears to be connected with the presence of a definite combination of foreign ions in the solution. Thus Na_2SO_4 is effective, but other sulphates, as $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , TiSO_4 , hydroxylamine sulphate and quinine sulphate, are ineffective. Similarly, phosphates other than the specific ones mentioned are ineffective. If the effect was dependent on the SO_4 , PO_4 , BO_3 , etc., ions as such, then all cosolutes affording these ions should be comparable in efficiency, just as OH is effective largely without regard to the particular cosolute affording it. A complicating factor enters in that the degree of ionization of the cosolutes in the NaF solution, and the effect that this has on the adsorption, is unknown.

4. In a series of acid salts of the effective cosolutes, the effectiveness decreases with increasing acidity. The following sequences were observed:



This behavior also suggests the adsorption of a specific compound, i.e., the normal salt, or a compound containing the normal salt such as the double-salt, $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$. The decreasing effectiveness with increasing acidity would then reflect the smaller concentration of normal salt available in the solution. However, ionization effects, as noted in 3 above, may also be involved.

5. The present cosolutes are distinguished as a group by the fact that they form double-salts with NaF. These double-salts are closely related in the geometry and dimensions of their lattices to NaF. The double-salts themselves can be crystallized out from the NaF solutions at high cosolute concentrations. Compound formation of this type is lacking with the OH-affording cosolutes, and with the ineffective cosolutes in general.

TABLE 6. COSOLUTES EFFECTIVE WITH NaF, CONTINUED.
DOUBLE-SALT-FORMING TYPE*Cosolute concentrations given in mols per mol NaF. Liminal concentration for {111} is between limits given.*

	R_2PO_4	R_2HPO_4	RH_2PO_4	R_2SO_4	$RHSO_4$
Na	111 > .003 100 < .0004	111 ^a > .11 100 < .02	100 ^b > .3 100 < .15	111 ^d > .12 100 > .001	100 < .2
K	111 > .02 100 < .0006	111 > .06	111 at .7° 100 < .037	111 > .03	111 > .75 100 < .3
NH ₄		100 ^b at .3 100 < .15	100 ^b at .17 to .35	100 ^e < .3	100 < .17
NaNH ₄ HPO ₄ : cubo-octahedra at .2 Na ₂ HAsO ₄ : 100 < .2 NaBrO ₃ : 111 > .3, 100 < .15 H ₃ BO ₃ : 110 from .65 to 3.0, 100 from .4 to .03					
Na ₃ AsO ₄ : 111 > .4, 100 < .18 Na ₃ VO ₄ : 111 at .27 KBrO ₃ : 111 > .25, 100 < .03					

^a With small 100 modifying faces.^d Cubes with small 111 at .015.^b With small 111 modifying faces.^e Some with very small 111 faces at .3.^c Cubo-octahedra at 0.3.

It appears from the foregoing considerations that the adsorption, if the habit variation is so ascribed, cannot be referred to an iron-substitution mechanism such as found with OH ion and NaF and, earlier, by Buckley with RO₄ ions and oxysalts. An interpretation of the habit variation consistent with the observed and inferred relations is found, however, from the general point of view of Bunn, and is described on the following pages.

MECHANISM OF THE HABIT VARIATION

Structural Control of Double-Salt Formation. The correlation between compound formation and habit variation noted in 5, above, recalls the findings of Retgers (11) and of Orloff (12), to whom most of the earlier work on habit variation in the alkali halides is due. These experimenters concluded that the habit-varying effect which a cosolute had for an alkaline halide did not rest in the cosolute itself, but in its ability to form double-salts with the halide. The actual mechanism by which the habit variation was effected was not explained.

The underlying reason for the correlation has become apparent through the work of Seifert (13) on the theory of double-salt formation. Habit variation is a concomitant of structural relations between solute

and cosolute which determine, in the first place, the formation of a double-salt between these substances. Seifert has shown that a large class of double-salts have what may be termed sandwich structures, in which the several components of the double-salt may be recognized as discrete layers periodically alternating in the structure. The Mg_2SiO_4 and $\text{Mg}(\text{OH}, \text{F})_2$ layers in the minerals of the humite group and the Al_2SiO_5 and $\text{Fe}(\text{OH})_2$ layers of staurolite illustrate the principles of the arrangement. According to Seifert, double-salts are formed from solutions that contain two compounds (solute and cosolute as here spoken of) which are structurally related and which are present in proportions at or near the required stoichiometric proportions for the double-salt. Under these circumstances the two compounds may intercrystallize along the planes of structural resemblance, affording the regularly stacked layers which compose the structure of the double-salt.

In illustration, the formation of the double-salt $\text{KPbCl}_2 \cdot \text{H}_2\text{O}$ from KCl and PbCl_2 , as shown by Mehmel and Nespital (14) and, later, by Seifert, is conditioned by the identity of arrangement and spacing of Cl^- in the $\{323\}$ and $\{121\}$ planes of the double-salt with the $\{111\}$ Cl^- planes of KCl . If, in the crystallization of the double-salt, the Pb^{++} concentration is decreased relative to K^+ and Cl^- , a point is reached at which KCl appears and crystallizes in oriented fashion upon the earlier formed double-salt crystals. The law of orientation is $(111)_{\text{KCl}} // \{323\}_{\text{D-S}}$ and $(11\bar{1})_{\text{KCl}} // \{\bar{1}21\}_{\text{D-S}}$, in which $\{323\} \wedge \{\bar{1}21\} \sim (111) \wedge (11\bar{1})$. The KCl crystals formed in this stage are *octahedra*. As the Pb^{++} concentration is further decreased the KCl forms *cubes*. The KCl crystals contain a small amount of Pb^{++} .

Habit Variation in NaF by Adsorption of Double-Salts. The variation in habit of NaF in the presence of the double-salt-forming alkali sulphates, phosphates, etc., is believed to be a consequence of the attachment (adsorption) of double-salt molecules, or of normal salt molecules, to the surface of the growing NaF crystals. This takes place under the impetus of the same forces which act in compound formation. The process can be viewed as a surface chemical reaction resulting in the formation of an "anchored" double-salt phase, in which the NaF part, or layer, of the double-salt is constituted by the surface ion-layers of the NaF crystal. The tendency for the formation of such a layer, and hence the strength of the adsorption, must increase as the solution (solute-cosolute system) approaches the phase boundary of the double-salt (e.g., KCl and PbCl_2). The outer portion of the double-salt layer is necessarily relatively mobile, but must tend for an ordered arrangement among its separate units in response to the same urge for a stable configuration that is expressed, at the proper cosolute concentration, by the formation

of actual crystals of the double-salt. The most stable arrangement and spacing would be that obtaining in crystals of the double-salt itself, or more specifically, since only two-dimensional or surface arrangements are involved, that obtaining in the growth surfaces of crystals of the double-salt. Accordingly, adsorption is facilitated upon any plane of the NaF which stands in structural relation to the double-salt, and that plane may thereby have its growth rate reduced sufficiently to cause it to appear on the NaF crystal.

Habit variation is not a necessary concomitant of the adsorption, but depends on the nature of the structural coincidences between the adsorbed substance and the crystallizing substance (NaF), and the crystal habits of the adsorbed and crystallizing substances. In general, habit variation may be expected (1) with an overall similarity of structure if the habits of the two substances are different, and (2) with a partial similarity in structure if the similarity is not in the normal habit of the crystallizing substance or in a vicinal plane of the crystallizing or adsorbed substances.⁴

The effect of the double-salt-forming cosolutes on the habit of NaF may now be considered from this point of view.



The crystallographic properties of the double-salts formed by these compounds with NaF are listed below.

$2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$. Isometric (15). Habit octahedral.

Isomorphous with the arsenate and vanadate analogues.

X-ray data (16): Face-centered cubic; space group $Fd\bar{3}c$; $a_0 = 27.86$; $N = 40$.

$2\text{Na}_3\text{AsO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$. Isometric. Habit octahedral.

Cell dimensions not known.

$2\text{Na}_3\text{VO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$. Isometric. Habit octahedral.

Cell dimensions not known.

The phosphate compound has a complete dimensional and geometrical analogue in NaF, with $a_{0\text{NaF}} = 4.619$ and $a_{0\text{D-S}} = 27.86$ where $27.86 = 6.0 \times 4.619$. Both lattices are face-centered cubic. Adsorption layers with a double-salt periodicity could hence form on any growth surface or plane of NaF regardless of indices. Crystals of the double-salt, however, are octahedral, and adsorption should therefore be favored on $\{111\}$ planes. This would induce an octahedral habit in the NaF, as is observed. The cell dimensions of the octahedral arsenate and vanadate double-salts are doubtlessly close to that of the phosphate compound, with which they are isomorphous.

⁴ For further discussion of some of these factors see Bunn, C. W.: *Proc. Royal Soc. London*, **141A**, 567 (1933).

Na₂SO₄

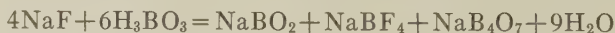
When Na₂SO₄ is present in relatively high concentrations in NaF solution the double-salt Na₂SO₄·NaF (*schairerite*) crystallizes out. With decreasing Na₂SO₄ concentration the NaF forms octahedra, skeletal cubes (due to hydrolysis of the Na₂SO₄) and, finally, at very low concentrations, simple cubes. The crystallographic properties of Na₂SO₄·NaF are described below.

Na₂SO₄·NaF. Natural crystals (*schairerite* (17)) are rhombohedral with large {10 $\bar{1}$ 1} and small {0001}, {10 $\bar{1}$ 1} and {10 $\bar{1}$ 3}. Artificial crystals are flattened on {0001} with {0223}, {10 $\bar{1}$ 1} and {10 $\bar{1}$ 3}; these crystals show evidence of cyclic twinning of individuals of lower symmetry and have been said (18) to become homogeneous (rhombohedral) only above 105°. X-ray Weissenberg study by the writer on a natural crystal of the composition Na₂SO₄·Na(F_{.81}Cl_{.19}) gave a hexagonal cell inconsistent with the morphology, with $a_0 = 12.12$, $c_0 = 19.19$, $z = 21$, $c = 2.67$ (calc.), 2.61 (obsvd.). A rhombohedral interpretation with c_0 tripled (space group $R\bar{3}m$) is consistent with the morphological orientation and ratio but is unproved.

A dimensional coincidence exists between the hexagonal nets {111} of NaF and {0001} of the double-salt, with the long diagonal of the former net = 2.1 times $d_{[1120]}$ in the latter. The actual dimensional relations are somewhat uncertain since the data for the double-salt refer to material containing Cl in substitution for F, with correspondingly larger cell dimensions, and possibly to an inverted hexagonal modification. As a consequence of this relation, the adsorption of double-salt from the solution would be facilitated upon {111} planes of the NaF, since the adsorbed material thereby approaches the stable {0001} configuration of its own crystals.

H₃BO₃

H₃BO₄ is of special interest in that it produces dodecahedra, sometimes modified by very small {100} and {111} faces, in NaF. H₃BO₃ and NaF react in water solution, but the nature of the reaction is little known (19). NaBO₂ and NaBF₄ are the principal products, and the reaction is approximately represented by the equation:



Complex double-salts between NaBO₂ and NaF have been reported but are considered mixtures (19). However, NaBO₂ forms a double-salt with NaCl as the mineral *teepleite*, NaBO₂·NaCl·2H₂O (20). Efforts to prepare the fluoride analogue of *teepleite* were unsuccessful.

Teepleite has a simple tetragonal lattice with $a_0 = 7.27$ and $c_0 = 4.84$. A resemblance is found in {110} of NaF to {110} of *teepleite*, the dimensions of these rectangular nets being 4.84×10.28 for *teepleite* and

4.619×3.266 for NaF where $3 \times 3.266 = 9.798$. A closer correspondence would obtain in the fluoride analogue of teepelite due to the smaller radius of F^- . It appears possible from this that the variation to dodecahedral caused by H_3BO_3 on NaF is due to the appositional adsorption of an unstable structurally-related double-salt on $\{110\}$ of NaF. Some support for this belief is found in that H_3BO_3 does not effect the habit of KCl or NaCl and does not react with those substances.

NaBrO₃

NaBrO₃ produces octahedra with weak anomalous birefringence in NaF. NaIO₃ and NaClO₃ are ineffective. Double-salts between NaBrO₃ and NaF are unknown, although NaBrO₃ forms a double-salt with NaBr, and NaIO₃ forms double-salts with NaI and NaCl (21). Structural coincidences appear to be lacking between NaBrO₃ and NaF, and the habit variation cannot be ascribed with reason to the double-salt type.

Structure-Apposition Adsorption in Halides other than NaF. Many instances of habit variation in alkali halides other than NaF are found to be in line with the theory of compound formation and adsorption under structural control described above.

NaCl forms a double-salt with NH₃ and crystallizes from liquid NH₃ as octahedra; KCl does not form a double-salt with NH₃ and crystallizes from liquid NH₃ as cubes (22).

Na₂SO₄ and Na₃PO₄ do not modify the habit of NaCl or KCl and do not form double-salts with those substances.

Urea changes the habit of NaCl to octahedral, as a consequence of the formation of the double-salt $CO(NH_2)_2 \cdot NaCl \cdot H_2O$ (23), and orients upon NaCl (2). On the other hand, urea does not affect the habit of NaF, KBr, KI and LiF, and does not possess structural coincidences or form double-salts with them.

KCl and KBr form double-salts with a number of di- and trivalent metallic halides and are often modified in habit by such substances. Retgers remarks in this connection that NaCl, on the other hand, has a much less marked tendency to form double-salts with the metallic halides and is rarely modified in habit by them.

Instances are also known of double-salt formation by the cosolute which are not accompanied by habit variation. Thus, $C_{12}H_{22}O_{11}$ and $C_6H_{12}O_6$ form double-salts with NaCl but do not cause habit variation in that substance. Retgers notes other exceptions. As already remarked, the occurrence of habit variation depends on the nature of the structural coincidences and on the habits of the substances concerned, which may be such as to cause selective adsorption by the normal (pure-solution) habit. Moreover, the structure of the compound formed may not be of

the sandwich-like double-salt type on which the preceding discussion is based.

DISCUSSION

The mechanism of habit variation in NaF based on the appositional adsorption of structurally related cosolutes illustrates the point of view of crystal-adsorption taken by Bunn. A minor point of difference is found in that Bunn relates the occurrence of adsorption to the impetus of mixed crystal formation, while the present instances take place under the impetus of compound formation. A few of the examples cited by Bunn, notably $\text{NH}_4\text{Cl} + \text{CuCl}_2$ and $\text{NaCl} + \text{urea}$, are to be referred to compound formation. Doubtlessly relations between a growing crystal and a cosolute other than mixed crystal or compound formation also give rise to structure-apposition adsorption. Compound formation is relevant to habit variation in NaF only in that it presages a particularly strong adsorption relation.

The mechanism of habit variation in NaF based on the substitutional adsorption of OH ion is essentially similar to the mechanism found by Buckley. This mechanism should also apply to other alkali halides for the adsorption of monovalent foreign ions which approximate in size to the cation or anion of the halide. The direction of habit variation in such instances should always be to octahedral. Appositional adsorption, on the other hand, may give rise to a variety of habits, according to the nature of the structural coincidences and the habits of the substances involved.

Influence of the Counter-Ion in Substitutional Adsorption. The nature of the foreign counter-ion in substitutional adsorption must also be of effect, although it does not play the essential role that it does in structure-apposition adsorption. It is well known that the adsorption of salts by colloiddally dispersed crystals is, as a rule, influenced by the nature of the counter-ion. The amount of the adsorption is frequently roughly paralleled by the solubility in the dispersion medium of the counter-ion—inner-ion compound. The influence of the counter-ion may be expected to be less marked with growing crystals than in colloidal systems, because of the dilution in the double-layer by the relatively large concentration of unlike crystal-ions of the same sign as the counter-ion of the cosolute.

Some observations by Buckley (24) on the substitutional adsorption of SO_4^- , CrO_4^- and SeO_4^- (as K salts) by growing KMnO_4 crystals are in line with a solubility effect. The strength of the adsorption, as evidenced by the efficiency in producing habit variation, is



which is the order of increasing insolubility of the K salts.

Increasing influence of the counter-ion must, in general, mark a transition from substitutional to structure-apposition adsorption. The crystallization of a substance in the presence of a cosolute which can enter into extensive solid solution in that substance, the counter-ions being identical, would represent an intermediate case.

ACKNOWLEDGMENTS

The writer is indebted to Professor Martin J. Buerger for discussions of the interpretative aspect of the investigation. Grateful acknowledgment is made to Mr. James Schulman and to Dr. Mortimer J. Bloom for discussions of the chemistry of several of the NaF-cosolute systems, and also to Mr. Schulman for the analysis of NaF cited.

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ICELAND SPAR IN NEW MEXICO

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DISCOVERY AND DEVELOPMENT

In 1931 while prospecting the ridge south of the Harding mine, Juan A. Brown of Dixon, New Mexico, unearthed a calcite deposit beneath two or three feet of overburden. Not realizing the character or possible worth of the deposit, its apex was blasted in order to open up and develop the property. The blasting shock undoubtedly ruined some of the near-surface Iceland spar in the deposit, but exposure in this manner revealed material of optical grade.

The deposit is located within the confines of the Copper Mountain Mining District in Section 31, T 23 N, R 11 E, Taos County, New Mexico. It is held under the Iceberg claim owned by Juan A. Brown and H. H. Bailey of Dixon, New Mexico. This claim lies parallel to and just south of the Lilac 1 on which is located the Harding mine, producer in the past of trimmed mica, lepidolite, and spodumene. The Iceland spar mine lies about 400 feet southwest of the Harding mine quarry, at an elevation of 7500 feet.

Although discovered as early as 1931, no appreciable development or production was attempted until May of 1939. Since then the deposit has been mined, under lease, in an open pit roughly 15 by 20 feet to a depth of 24 feet. During the last half of 1939 about 850 pounds of optical-grade material was mined, trimmed, and shipped. A considerable portion of this was taken by the Bausch and Lomb Optical Company. The largest single piece of optical-grade Iceland spar obtained from the deposit by the end of 1939 weighed five pounds and eight ounces. At the time of the study by the writer in November, 1939, perfect optical-grade cleavage rhombs of three to four inches on a side were exhibited.

Since the completion of this work Johnson¹ has published a brief note on the deposit as he saw it a few months after mining began in 1939.

GENERAL OCCURRENCE

The geology and occurrence of potential and commercial deposits of Iceland spar throughout the world have been briefly described by Hughes.²

From descriptions in this work, it is apparent that most of the Iceland spar has come from hydrothermal deposits in basaltic igneous rocks.

¹ Johnson, J., Harlan, Iceland spar in Taos County, New Mexico: *Am Mineral.*, **25**, 151-152 (1940).

² Hughes, H., Herbert, Iceland spar and optical fluorite: *U. S. Bureau of Mines, Information Circular* **6468** (1931).

Many, like the Helgustadir, Iceland deposit, are in basalt flows where the spar may have an origin similar to zeolites with which the Iceland calcite occurs in primary cavities in the rock or in larger replacement masses and veins. Such occurrences are usually accompanied by considerable alteration, a part of which may be secondary. This type of occurrence, from rather meager information, appears probable for the Cedarville, California deposit, a past producer, and for a non-commercial occurrence near Pyramid Lake, Nevada. A similar occurrence in basic rock, diabase, is reported in the Kenhardt district, northwest Cape Province, South Africa. This deposit has replaced the Iceland source in recent years and has supplied a considerable portion of the European and domestic demand.

Except for the Iceland deposits, few detailed studies or descriptions of the paragenesis of Iceland spar veins have been found available by the writer. The Greycliff, Montana, deposits were described by Parsons³ from a report by Dr. S. C. Lind of the U. S. Bureau of Mines. From the descriptions these deposits appear to be rather persistent fissure veins in a country rock of gneiss. This occurrence more nearly resembles the New Mexico deposit from the point of associated country rock. In both of these cases, however, the nature of the country rock has little genetic relationship to the vein material. On the other hand, it appears probable that basaltic flows or intrusives may have some genetic relationship with pure calcium carbonate solutions capable of forming Iceland spar deposits. But until more detailed and specific descriptions are made of Iceland spar deposits from other localities, such as those listed by Hughes⁴ in Spain, Spitsbergen, Argentina, British Columbia, and other little known occurrences, any statements as to the genetic relationships of Iceland spar are necessarily tentative and without weight. To summarize, however, the known occurrences to date have fallen into two groups: (1) in basaltic igneous rocks and (2) in fissure veins where the nature of the country rock is of little or no importance. It may be of some significance that Iceland spar has not been described or produced from contact metamorphic calcite, nor from cavernous calcite as in the Tri-State deposits.

NEW MEXICO OCCURRENCE

Geologic Setting. In the vicinity of the Iceland spar deposit and the Harding Mine, the rocks consist of hornblende schists and quartzites. Just⁵ has mapped and termed these rocks the Hopewell series of Protero-

³ Parsons, Chas. L., Iceland spar in Montana. *Science, New Series*, **47**, 508-509 (1918).

⁴ *Op. cit.*, pp. 8-12.

⁵ Just, Evan., Geology and economic features of the pegmatites of Taos and Rio Arriba Counties, N. M.: *New Mexico School of Mines, Bull.* **13**, 21 (1937).

zoic (?) age. He found that these rocks were originally a part of a volcanic and sedimentary series which consisted of andesite and basalt extrusives. (Picuris basalts) intercalated with some clastic sediments. The Hopewell series in this area forms a narrow belt of from one-quarter to one mile in width trending about N 70° E. This belt is part of the south limb of a syncline which plunges westward. The series is the oldest of the Proterozoic (?) mapped in the general area. To the south of the deposit, a distance of about one-quarter of a mile, the schists and quartzites are intruded by the Dixon granite which Just⁶ has tentatively dated as late Proterozoic (?) (Killarney) age.

The Iceland Spar Deposit. The Iceland spar forms a lenticular, pipe-like deposit which lies nearly parallel to the schistosity of the Hopewell series. The footwall of the deposit dips S 45° E at 73°. The vein has a length of about 30 feet at the surface and a maximum width of nine and a half feet near the center. Johnson⁷ states that the deposit appears to plunge to the southwest. Since the deposit was not opened up to the end in this direction, it is difficult to see how this conclusion was reached. At the time of the study by the writer the northeast end was completely exposed and the pitch of the vein in this direction was clearly seen as shown in Fig. 1.

The walls of the vein are coarsely brecciated and altered for a width of from one to three feet. The alteration probably extends to a slightly greater distance into the wall than the brecciation. The breccia fragments on the whole consist of angular, altered schistose blocks, one to two feet in diameter. In the northeast end of the breccia sheath are blocks of quartzite derived from the end of a quartzite lens in the schist series. This quartzite bed widens from a foot or so in the northeast end of the vein to 10–15 feet on the top of the low ridge some 50 feet northeastward along the strike.

The alteration of the breccia zone adjacent to the vein has produced a softened, brownish to yellowish green mass. Under the microscope the hornblende of the schist is seen to be altered to biotite, golden yellow (bleached) biotite, limonite, and kaolinitic material. The quartzite blocks along the northeast end of the vein have been replaced in patches and veinlets by ankerite which has been later surficially altered in part to limonite.

About 50 feet southwest of the vein, the hornblende schist is much altered to epidote. Just⁸ reports epidotization of the hornblende schists as a contact metamorphic effect near the Dixon granite a short distance

⁶ *Op. cit.*, p. 24.

⁷ *Op. cit.*, p. 151.

⁸ *Op. cit.*, p. 25.

to the south. Some bleached epidote occurs in the altered breccia zone which might be taken as part of the wall-rock alteration genetically as-

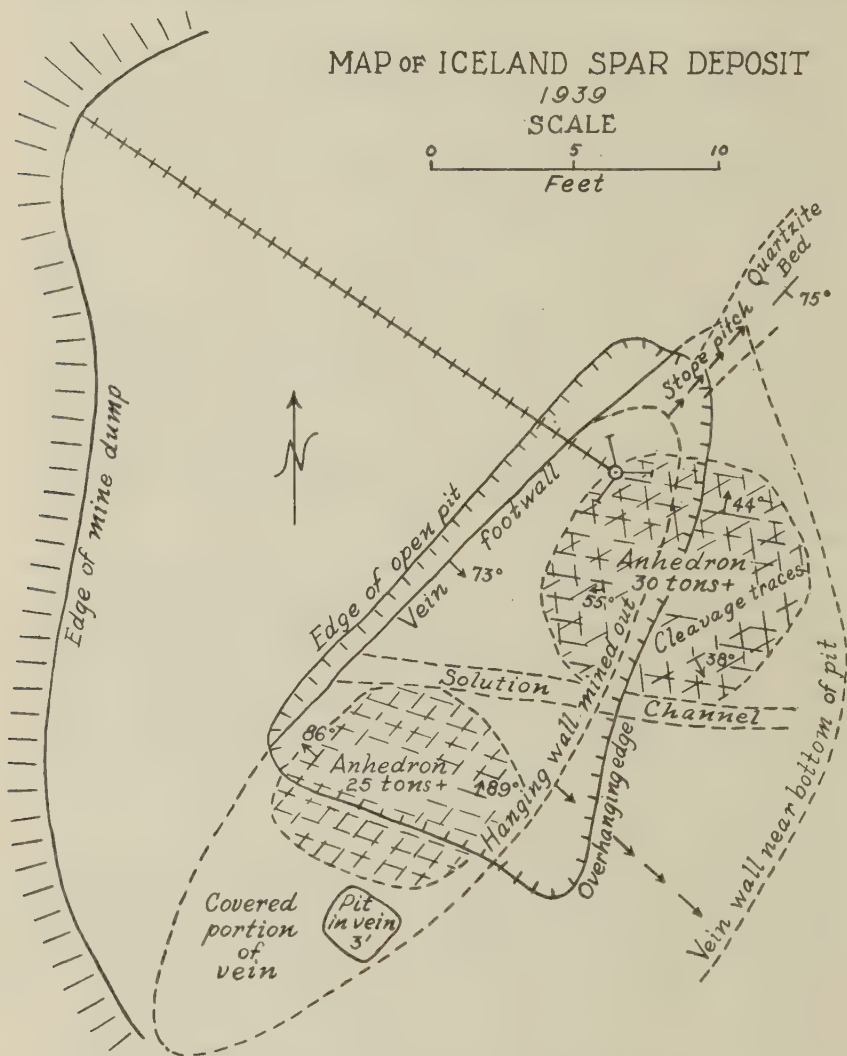


FIG. 1. Map of Iceland spar deposit.

sociated with the calcite deposition. However, it is probable that such epidote was earlier and was incorporated only by chance in the breccia and alteration zone which accompanied the calcite vein formation.

The vein proper is composed almost entirely of exceedingly coarse anhedral calcite. No euhedral calcite is present. Several small solution cavities were encountered in the top of the deposit. These were mostly filled with surficial kaolinitic material. One larger solution cavity or "water-course" across the vein persists to the mined depth as shown in Fig. 1. A few lentils or inclusions of highly altered schist were found in the vein.

The edge of the vein is quite irregular in detail. Small blunt offshoots of the calcite protrude into the breccia wall. Some of these are still left as isolated patches in the hanging wall. They appear as replacements of individual breccia fragments.

A few other minerals occur in the calcite in very minor quantities. Chalcopyrite replaces the calcite in irregular and disseminated veinlets. Associated with the chalcopyrite is a fine, granular, greenish calcite. The chalcopyrite occurs as tetragonal scalenohedrons imbedded in the spar and in the greenish granular calcite. The chalcopyrite is mostly surficially altered to chrysocolla, tenorite, and limonite. The greenish color of the granular calcite is due to chrysocolla and it is possible that the granular calcite is supergene.

Calcite. Three types of calcite occur in the deposit. The most abundant type is white calcite. Next in abundance is the clear, colorless calcite from which is culled and trimmed the optical spar. The third type is a banded pink calcite. When the pink calcite was first found it was thought to contain lepidolite because of the similarity in color and the proximity to the lepidolite-bearing pegmatites of the Harding mine. Nearly all gradations between these three calcites occur in the vein.

The pink material in the calcite is always in fuzzy, closely spaced bands or layers which are only a fraction of a millimeter thick. The bands are not twin lamellae. They are due to a "salt and pepper" scattering of very small colloidal particles or aggregates of particles, averaging about .05 millimeter in size, which are aligned along definite crystallographic planes.

The more common banding is parallel to the rhombohedral cleavage. The only other banding, although not as common, is parallel to the scalenohedron $21\bar{3}1$. This was determined by grinding a face parallel to the banding in question and measuring the interfacial angle between the ground face and the cleavage face. This checked by repeated contact goniometer measurements with the interfacial angle $(10\bar{1}1 \wedge 21\bar{3}1)$ of $29^{\circ}02'$.⁹

Cleavage pieces are often pink, banded in one sector and clear in the remainder. The banding terminates irregularly in some specimens al-

⁹ Whitelock, Herbert P., *Calcites of New York: New York State Museum, Memoir 13*, 73, 77 (1910).

though in others it ends evenly along planes such as those of the scalenohedron. Banding parallel to both the rhombohedral and scalenohedral directions in different sectors of a single cleavage piece sometimes occurs. The pink banded material is more closely associated with the Iceland spar type of calcite.

Much of the calcite of all three types is twinned. Much of the otherwise optical-grade Iceland spar is of no value for this reason. The twins are of two well known types. Large individual twins occur twinned on *c* or parallel to (0001). The most common twinning is polysynthetic parallel to (01 $\bar{1}$ 2). Parting planes parallel to this direction are prominent.

One of the most unusual features of the calcite, noticed principally in the colorless and pink types, is the existence of a perfect conchoidal fracture. This perfect glass-like fracture was found in several pieces on the dumps and was subsequently developed on several occasions in the laboratory. Dana¹⁰ mentions this fracture as "obtained with difficulty" because of the excellent rhombohedral cleavage.

In order to discover the impurities in the pink calcite, spectrographic analyses were made of it and the Iceland spar. These analyses were made by Mr. Guy V. Martin, Martin Laboratories, Albuquerque, N. M. Samples of the two calcites and Baker's c. p., calcium carbonate were compared, with results as follows:

Sample	Mg	Fe	Mn	Si	Al
Baker's c.p. CaCO ₃	0.3	0.003	t	0.002	t
Iceland spar	t	0.001	0.01	t	t
Pink spar	0.1	0.01	0.02	.001	0.001

t—spectrographically present; less than 0.0005.

The results for the pink spar are an average of two samples—one of average pink and another so strongly pigmented as to be almost brown.

From these results it is seen that the material pigmenting the pink calcite so strongly is present in only very minute quantities. Both the pink calcite and the Iceland spar are purer than the Baker's c. p., calcium carbonate.

Both manganese and magnesium are present in the Iceland spar as well as in the pink spar. Why then is the Iceland spar not colored since both iron and manganese are present? The greatest difference lies in the iron

¹⁰ Dana, J. D., *System of Mineralogy*, 266 (1909).

content, and possibly the iron is the principal cause of the pink color. Manganese, however, is commonly thought to give rise to pink color in carbonates such as rhodochrosite. Perhaps a significant difference in the

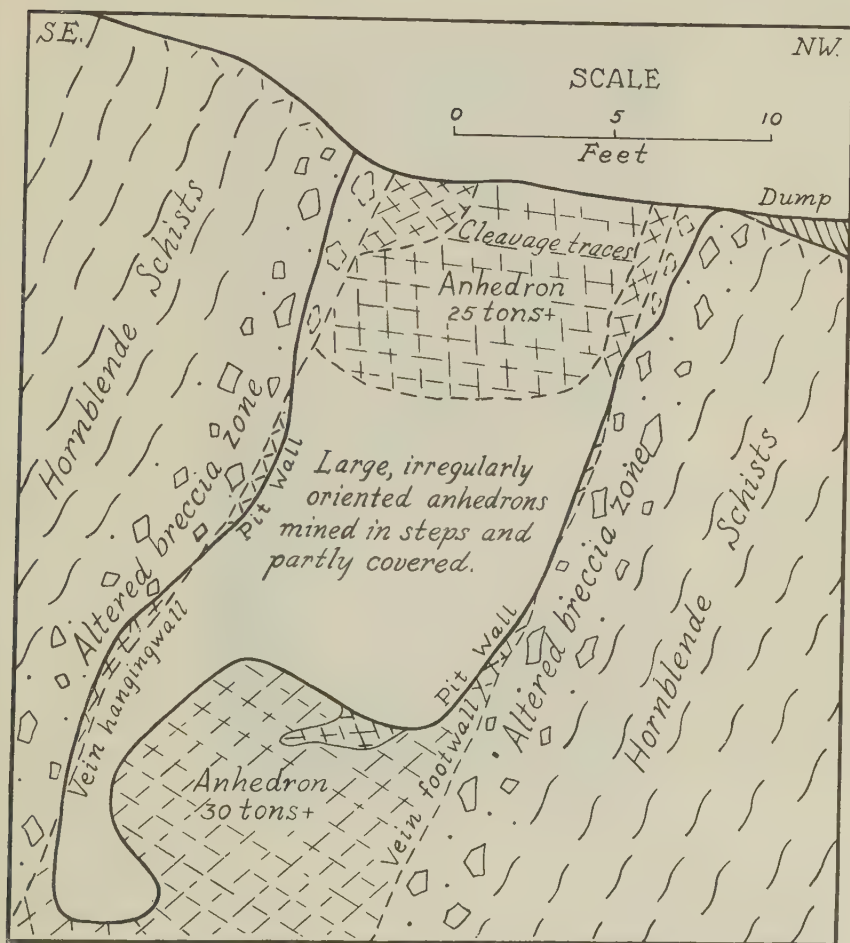


FIG. 2. Cross section of Iceland spar vein showing orientation and position of large anhedronal crystals.

composition of the two calcites is the presence of silicon and aluminum in the pink spar and their absence in the Iceland spar. The explanation put forth partly at the suggestion of Mr. Martin is that the silicon and aluminum in colloidal form tend to localize or retain the manganese and iron pigments in a manner which brings out the color.

Some banded pieces observed under a binocular show very tiny dendritic growths of the pink material more or less normal to the planes of banding. These are suggestive of the "silicate gardens" produced by soluble compounds absorbed in silicate gels.

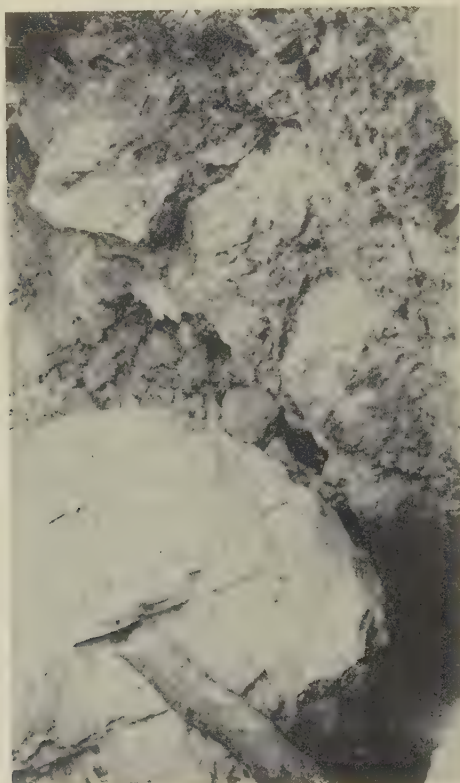


FIG. 3. View of large anhedron of calcite weighing 30 tons or more near the bottom of the open pit. Note the large breccia fragments in the hanging wall of the deposit.

Pycnometer specific gravity determinations of the Iceland spar and pink banded calcite were made for reference. The following are values obtained at room temperature:

Iceland spar.....	2.716
Pink spar.....	2.721

Large Crystals. Although the vein as exposed is rather small, some of the crystals are gigantic. Portions of two very large crystals were exposed on the side and bottom of the pit at the time of study by the writer. The larger of these occurred practically at the surface with cleavage traces oriented as shown in Fig. 2. The southwest side of the pit (Fig. 1) coin-

cided with the third rhombohedral cleavage direction which was vertical with strike S 72° E. The top of this crystal had been partly eroded away. The crystal extended into the southwest wall for at least two feet at the top. About six feet of the crystal had been mined away on the northeast side. The more striking anhedral crystal occurred in the bottom of the pit with the *c*-axis nearly vertical as shown in Fig. 2. This crystal was exposed on three sides including a portion of the underside. Some of the exterior of the crystal had been stripped off by mining. Before the end of 1939 the entire crystal was removed but a very good idea of its size and position can be obtained from Fig. 3. From the dimensions of the remaining crystal at the time of the study it is estimated to have weighed at least thirty tons, or possibly as much as forty tons before it was partially mined. Both of these crystals rank second in size to the large Iceland crystal described by Des Cloizeaux and recorded by Palache.¹¹

Origin. Points to be considered in connection with the genesis of the Iceland spar deposit are: (1) the brecciation zone in the wall rock, (2) the nature of the wall rock alteration, (3) the purity of the calcite, and (4) the pink banding of the calcite.

The brecciation is spacially and genetically related to the calcite vein. It is a peripheral zone about the vein and has no extension beyond a few feet in any direction from the vein. The breccia is a mechanical one rather than a replacement breccia. It is not a fault breccia as indicated by Johnson,¹² and little or no slickensiding is present. The volume of the breccia as compared to the size of the vein is large as in many breccia pipes. Thus the channelway for the carbonate solution appears to have been produced by rapidly released gaseous emanations which moved upward from depths along the foliation of the hornblende schists. A small lenticular, pipe-like channel produced by such means would be clogged by large angular blocks torn from the walls. At least locally, the void space might be considerable.

The gaseous emanations producing the pipe were probably in part responsible for the alteration of the brecciated wall rock. However, some of the alteration, if not a major portion, was produced by the carbonated solutions which later deposited the calcite. Some supergene kaolinization was effected in the top of the alteration zone. This is whitish in color in contrast to the green coloration of the altered wall rock deeper in the deposit.

Because of the difficulty encountered in a mineralogic and petrographic study of the altered rock, spectrographic analyses were made of the

¹¹ Palache, Charles, The largest crystal: *Am. Mineral.*, **17**, 362-363 (1932).

¹² *Op. cit.*, p. 152.

material. These investigations indicate rather clearly the hypogene nature of the wall rock alteration. Several analyses were made of typical unaltered hornblende schist adjacent to the walls of the deposit. Several similar analyses were also made of the various stages of altered wall rock. By comparison with the unaltered rock, the altered material showed additions of *nickel*, *barium*, *bismuth*, *chromium*, and *molybdenum*. The presence of these elements in the altered rock and their absence in the original wall rock precludes any probability that the alteration was supergene.

Was the calcite of the vein deposited by filling of a cavity already present or by replacement of much brecciated material, or by both processes? The deposit shows no characteristics of cavity filling such as crustification, banding, or primary vugs. However, recrystallization could have obliterated such primary structures. Some filling of space in the breccia pipe must have occurred since a pipe so conceived would in all probability contain numerous super-capillary openings. It might be suggested that the very purity of the calcite should indicate an origin by filling of an open cavity or pipe because replacement would contaminate the solution so as to prevent deposition of pure calcite. But this is in effect proposing that host minerals cannot be replaced without leaving some trace in the metasome, or that replacement cannot be complete. If purity of a vein or a mineral be used as a criterion of cavity or fissure filling, then all veins of pure quartz, pure calcite, pure pyrite, etc., must be of such origin. A criterion of this nature would relegate replacement to a minor role in mineral deposition. In spite of purity of the calcite it is believed that replacement was the principal mode of deposition of the vein, although filling of the void space present in the pipe necessarily took place.

The origin of the pink material in the banded calcite is a problem. It appears to be easily explained as a paragenetic intergrowth. If all of the pink material were confined to crystallographic planes such as that of the unit rhombohedron and the scalenohedron ($21\bar{3}1$) a paragenetic origin might be indicated. However, a few specimens show pink material along conchoidal fractures. This seems to indicate a later introduction of the colloidal pink material. If the pink material showed a spacial relation to the surface it might even be supergene. Since it does not, a primary hydrothermal infiltration of the material into the calcite subcapillary pores paralleling the principal crystallographic directions seems to be the appropriate explanation.

By way of conclusion and summary, the deposit is of hydrothermal origin. The mineral channel was formed by vigorous gaseous escape from depths, which formed a lenticular breccia pipe parallel to the schistosity of the country rocks. Wall rock alteration was initiated at the time of brecciation and continued until the calcite deposition. The calcite dep-

osition was accompanied by replacement of breccia fragments which filled the pipe. That the wall rock alteration and calcite deposition were both hypogene is indicated by such metals as nickel, chromium, and molybdenum in the rock and chalcopryrite veinlets in the calcite. If any usual evidences of fissure filling existed, they were early obliterated by recrystallization and incorporation of smaller crystals into the larger anhedrons. Late hypogene infiltration of colloidal pigmenting impurities gave rise to the banded calcite.

IDENTIFICATION OF THE COMMONER TELLURIDES

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INTRODUCTION

This paper is based on a study of one hundred polished sections from the La Plata, Colorado mining district, twenty-five sections from the Eastern Ontario gold area, and twelve sections from Cripple Creek, Colorado. The writer wishes to express his thanks to Mr. E. B. Eckel of the U. S. Geological Survey for the use of the La Plata collection, to Mr. R. D. Hoffman, Mining Geologist, New York City, for the specimens from Cripple Creek, and to the managements of the Lake Shore, Toburn, Wright-Hargreaves, Macassa and Dome mines for the specimens from those properties. The writer is especially indebted to Dr. M. N. Short of the University of Arizona for helpful criticism and permission to use the data which appears in his "Microscopic Determination of the Ore Minerals," *U. S. Geological Survey, Bulletin 825*, 1931.

IDENTIFICATION OF THE TELLURIDES

Considerable difficulty attends the identification of the tellurides. In hand specimens the bright silvery-white color is exhibited by a number of other minerals, and the relatively small amount of material present, in even high grade ore, is usually insufficient for satisfactory physical, blowpipe, and ordinary wet chemical tests. The simplest test is the cherry-red color imparted to hot concentrated sulphuric acid by a fragment of a telluride mineral, but the writer has found that with very small amounts of material this test is not always reliable.

The most satisfactory method of identification of the tellurides is by means of chemical and etch tests on polished sections of ores under the reflecting microscope. The technique and application of this method are fully described by Short.¹ In his systematic scheme of identification the unknown is first treated with standard etch reagents, which closely determine the position of the unknown in the determinative tables. Microchemical analysis is then used when necessary to confirm the identity of the mineral.

It has been the writer's experience that etch tests on tellurides are not particularly reliable, due probably to the fact that it is rarely possible to place a drop of reagent within the area occupied by a single telluride mineral. It seems better therefore, when working with ores known to con-

¹ Short, M. N., Microscopic Determination of the Ore Minerals: *U. S. Geol. Survey, Bull. 825* (1931).

tain tellurides, to first make the microchemical tests for tellurium on a likely unknown, which may be followed by additional microchemical or etch tests. In any case confirmatory microchemical tests should be made to insure positive identification.

Additional difficulty is encountered in the case of tellurides containing both gold and silver. Sylvanite, calaverite and krennerite are so nearly identical in composition that on many specimens the usual etch and microchemical tests described in *Bulletin 825* will not differentiate between them. Identification can be accomplished by the application of concentrated HNO_3 with subsequent development of characteristic etch cleavage as described by Short.² The writer has found that the reaction of concentrated nitric on other tellurides than those above is highly characteristic and materially aids in their identification.

DESCRIPTION OF THE TELLURIDES

A compilation of the distinguishing characteristics of the commoner tellurides follows.

Altaite— PbTe

Color, galena white; hardness B; nearly sectile. Isotropic, but some specimens exhibit weak anomalous anisotropism. Cubical cleavage is prominent in most specimens, as exhibited by two sets of cleavage cracks at right angles, but does not show triangular pits like galena.

HNO_3 (1:1) —Effervesces vigorously and stains dark gray.

HCl —Some specimens effervesce vigorously and turn black, others tarnish iridescent, still others are negative.

KCN —Negative.

FeCl_3 —Quickly stains iridescent.

KOH —Negative.

HgCl_2 —Negative.

HNO_3 (Conc.) Stains iridescent.

Altaite gives strong microchemical tests for lead with potassium iodide, and for tellurium with cesium chloride.

Calaverite— $(\text{Au}, \text{Ag}) \text{Te}_2$

Color, light yellow to pinkish-white; hardness C. Strongly anisotropic, polarization colors are light gray, brown, dark gray. Some specimens show multiple twinning.

HNO_3 (1:1) —Effervesces faintly, surface stains either creamy-brown or iridescent, then black. After acid is washed off a shingly etch cleavage, usually with little or no parallelism, appears.

HCl —Negative.

KCN —Negative.

FeCl_3 —Most specimens are negative, some stain a light brown.

KOH —Negative.

HgCl_2 —Negative.

HNO_3 (Conc.) Stains creamy-brown. After acid is washed off a parallel etch cleavage appears in one direction only.

² Short, M. N., Etch tests on calaverite, krennerite and sylvanite: *Am. Mineral.*, **22**, 667-674 (1937).

Calaverite gives a good microchemical test for silver with potassium mercuric thiocyanate, but the reaction with potassium bichromate may be negative. It gives strong tests for gold with pyridine-HBr solution and for tellurium with cesium chloride.

Coloradoite— HgTe

Color, light pinkish gray; hardness C, appears sectile in small grains. Isotropic.

HNO_3 (1:1) —Most areas negative, some slowly stain light brown to iridescent.

HCl —Most specimens negative, others slowly stain dark gray to black.

KCN —Negative.

FeCl_3 —Stains differentially, iridescent.

KOH —Negative.

HgCl_2 —Negative.

HNO_3 (Conc.) Some specimens stain iridescent, others negative.

Coloradoite gives strong microchemical tests for mercury with cobalt nitrate and potassium thiocyanate, and for tellurium with cesium chloride. The mineral must be taken into solution with fresh aqua regia and the microchemical test for mercury should be run on a known mineral until the technique of this test is perfected.

Hessite— Ag_2Te

Color, light gray; hardness A; nearly sectile. Most specimens are strongly anisotropic and show multiple twinning; polarization colors white, steel-blue, bornite-pink. The writer has never seen a specimen of isotropic hessite and the isometric character is open to question.

HNO_3 (1:1) —Most specimens stain quickly black without effervescence, some stain lightly iridescent.

HCl —Slowly stains black, some areas are negative.

KCN —Some specimens slowly stain black; action usually requires more than one minute and on some specimens is negative.

FeCl_3 —Quickly stains iridescent.

KOH —Negative.

HgCl_2 —Stains brown to iridescent.

HNO_3 (Conc.)—Stains dark gray.

Hessite gives strong microchemical tests for silver both with potassium mercuric thiocyanate and potassium bichromate, and for tellurium with cesium chloride. The mineral closely resembles argentite in polished section, but as it is not completely sectile will yield a powder upon scratching, whereas argentite yields only metallic shavings.

Krennerite— $(\text{Au}, \text{Ag})\text{Te}_2$

Color, creamy white; hardness C. Strongly anisotropic, polarization colors light gray, yellow, brown. Some grains show multiple twinning.

HNO_3 (1:1) —Effervesces weakly to strongly and stains creamy-brown to dark brown. When acid is washed off a shingly etch cleavage, usually with little or no parallelism, may appear. Some areas give a good etch cleavage in two directions.

HCl —Negative.

KCN —Negative.

FeCl_3 —Stains light yellow.

KOH —Negative.

HgCl_2 —Negative.

HNO_3 (Conc.) Stains creamy-brown. When acid is washed off a parallel etch cleavage appears in two directions at right angles to one another, giving a brick-like pattern.

Krennerite gives a good microchemical test for silver with concentrated NH_4OH , but the reaction with potassium bichromate may be negative. It gives strong tests for gold with pyridine-HBr solution and for tellurium with cesium chloride.

Petzite— $(\text{Ag}, \text{Au})_2\text{Te}$

Color, galena white; hardness A; nearly sectile. Isotropic.

HNO_3 (1:1) —Quickly stains iridescent to dark gray, usually without, but on some specimens with faint effervescence.

HCl —Some specimens stain iridescent, others negative.

KCN —Some specimens negative, some slowly stain light brown.

FeCl_3 —Quickly stains brown.

KOH —Negative.

HgCl_2 —Slowly stains brown.

HNO_3 (Conc.) Stains dark brownish-bronze. After drop is washed off, an irregular shingly etch cleavage without parallelism appears on most specimens.

Petzite gives a strong microchemical test for silver with potassium mercuric thiocyanate; with potassium bichromate the test may fail, but with care can usually be obtained. It gives strong tests for gold with pyridine-HBr solution and for tellurium with cesium chloride. Although nearly sectile, like hessite, it is much lighter in color and may exhibit less perfect cubical cleavage and triangular pits than galena. It is a much rarer mineral than hessite.

Sylvanite— $(\text{Au}, \text{Ag})\text{Te}_2$

Color, silvery-white to creamy-white, lighter than calaverite; hardness C. Strongly anisotropic, with multiple twinning; polarization colors light gray, brownish-gray, dark gray.

HNO_3 (1:1) —Stains iridescent. Some specimens effervesce faintly, others do not. A parallel etch cleavage in one direction only appears before the acid is washed off.

HCl —Negative.

KCN —Negative.

FeCl_3 —Most areas negative, some stain light yellow.

KOH —Negative.

HgCl_2 —Negative.

HNO_3 (Conc.) A parallel etch cleavage in one direction only appears before the acid is removed.

Sylvanite gives a good microchemical test for silver with potassium mercuric thiocyanate, but the test with potassium bichromate may be negative. It gives a strong test for gold with pyridine-HBr solution and for tellurium with cesium chloride.

Tellurium—Te

Color, silvery-white, somewhat lighter than krennerite and calaverite, distinctly lighter than hessite; hardness B. Strongly anisotropic, polarization colors light to dark gray.

HNO_3 (1:1) —Stains black with vigorous effervescence.

HCl —Fumes tarnish some areas, others negative.

KCN —Negative.

FeCl_3 —Slowly stains light brown or yellow. Action weak and on some specimens practically negative.

KOH —Negative.

HgCl_2 —Some specimens stain light brown, others negative.

HNO_3 (Conc.) Stains light brown to iridescent.

NOTES AND NEWS

GOLDSCHMIDTINE IDENTICAL WITH STEPHANITE

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Goldschmidtine was recently described (1939) as a new mineral occurring at Andreasberg, Harz, in orthorhombic crystals with the composition Ag_2Sb . To test the homogeneity of the crystals two polished sections were made, one of a typical crystal group, the other of a portion of the sample of crystal fragments used for the analysis. These sections showed only one mineral. X-ray powder photographs on samples drilled from the sections gave a pattern unlike that of dyscrasite— Ag_3Sb , the name attached to the specimen on which the orthorhombic crystals were found.

More recently Dr. G. A. Harcourt of the International Nickel Company wrote me that he had re-examined the polished sections and powder photographs of goldschmidtine and had found that they are indistinguishable from sections and photographs from two specimens of stephanite— Ag_5SbS_4 from Freiberg, Saxony. Dr. Harcourt also pointed out that the remaining properties given for goldschmidtine agreed with those of stephanite, except the specific gravity and the composition. The corresponding essential data compare as follows:

	GOLDSCHMIDTINE		STEPHANITE
	Analysis	Ideal	Ideal
Ag.....	64.78	63.9	68.5
Sb.....	35.01	36.1	15.2
S.....	0.06	—	16.3
$a:b:c$	0.6312:1:0.6860		0.6291:1:0.6851 (Vrba, 1886)
a_0, b_0, c_0	7.75, 12.32, 8.42 all $\pm 0.05 \text{ \AA}$		7.85, 12.48, 8.58 \AA
$a_0:b_0:c_0$	0.629:1:0.683		0.629:1:0.687 (Salvia, 1932)
Twin plane.....	(110)		(110)
Hardness.....	$2\frac{1}{2}$		$2-2\frac{1}{2}$
Specific gravity.....	6.83		6.2-6.3

Dr. Berman kindly redetermined the specific gravity of goldschmidtine with the torsion micro-balance, which was not available when the material was first studied; the new values, 6.26, 6.27, lie within the range given for stephanite. A new analysis on a small sample of clean crystals of goldschmidtine, by the International Nickel Company, yielded: Ag 68.1, Sb 14.4, S 15.6 ± 0.1 ; total 98.1, in good agreement with the compo-

sition of stephanite. It is clear, therefore, that the mineral described as goldschmidtine is in fact stephanite and that the name goldschmidtine must be withdrawn. By an unlucky chance a faulty analysis was compensated by an inaccurate specific gravity, giving an integral cell content and thus concealing the errors.

Since the mineral described as goldschmidtine is stephanite some points of interest may be salvaged from the description. The morphology of stephanite is in fair agreement with that attributed to dyscrasite in the older literature, but it bears no simple relation to the hexagonal structure found by Machatschki (1928) for natural and artificial dyscrasite. This suggests that the early measurements supposed to represent dyscrasite were actually made on associated crystals of stephanite.

In addition to the common and very evident twinning on (110) the crystals from Andreasberg show symmetrical striations on {110} suggesting twinning on (001). This twin law is established on stephanite which is therefore referred to the pyramidal class— $mm2$. Evidence was also found (Figs. 6 and 7) for twinning on (100). The absence of two symmetry planes limited the symmetry to the disphenoidal class—222. The x -ray extinctions noted, hkl with $h+k$ odd, $00l$ with l odd, are the same as those given for stephanite by Salvia. In the class 222 these extinctions admit only one space group, $C222_1$, which thus appears to be confirmed.

However, a new set of x -ray measurements on stephanite, recently made in this laboratory by Mr. E. D. Taylor of Laval University, revealed a further extinction condition which gives a unique space group in the class $mm2$ but is not compatible with the class 222. Without anticipating Mr. Taylor's interesting results, to be given in a forthcoming paper, the geometrical and röntgenographic results are reconciled by the following consideration, for which I am indebted to Professor J. D. H. Donnay: twinning on any one of the missing elements of symmetry in either of the merohedral orthorhombic classes gives one and the same twin orientation, and therefore the merohedral classes ($mm2$ and 222) cannot be distinguished by such twinning alone.

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MODELS OF TERNARY SYSTEMS

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Many students find it difficult to visualize ternary composition-temperature diagrams—often called ‘Bowen diagrams’—in the usual two-dimensional form. As a teaching aid, three-dimensional models of these diagrams are desirable, but are not obtainable commercially. The following is a brief description of the technique employed to make such models.

The two-dimensional ternary diagram, with the temperature contours of the liquidus surface, is enlarged to measure twelve inches on a side. This may be done with a visual optical device, or by photostat. The final diagram should be on light paper, so that an impression may be made through it on carbon paper, as described below.

Several equilateral triangles of $\frac{3}{8}$ " plywood, twelve inches on a side, are



FIG. 1. Set-up ready to cast positive, showing card for corner support.

FIG. 2. Completed model of system albite-anorthite-diopside, with device for drawing contours.

procured; for the ordinary model about fifteen of these will give the requisite vertical spread, or relief, between lowest and highest points in the temperature range. Each temperature contour is now marked on a triangle of plywood, by placing a sheet of carbon paper on the wood, superposing the enlarged diagram, and tracing the desired contour. These contours are cut out on a band saw, and the resulting pieces are nailed together in proper order to form a step model of the liquidus surface. Plasticine is used to fill up the steps and produce a smooth surface. The master positive model is now complete.

From the master positive, lightly greased, a negative in plaster of Paris is made. This in turn is used to cast the final positive.

Before pouring the final positive, the writer places a thin card, folded and creased, in each corner of the mold, as shown in Fig. 1. When the

positive has hardened, this card may be stripped off and a fresh card glued in the inset thus provided. This protects the edges, yet is flush with the sides of the model.

To prevent sticking of the final positive to the plaster negative, the negative surface is coated with 'label lacquer,' a solution of celluloid in acetone. If this is done no grease need be used, and the resulting positive surface is nearly perfect, requiring a minimum of scraping.

The plaster should be mixed all at once in a large container, to a rather fluid consistency so that it may be poured in one operation and smoothed off on the surface. Annoying airholes result from casting with stiff plaster.

The model is finished by shellacking and enameling, after which the binary diagrams on the sides, and the contours on the top, are inked in.

For drawing the contours the writer used the device shown in Fig. 2. Its support is a horizontal triangle on three legs. On this rests a movable unit consisting of three rods radiating from a vertical sleeve. A rod, to which a drafting pen is fastened, fits in this sleeve. The pen used is hinged and may be adjusted to work on a surface of any degree of inclination. The pen is held at the proper height by means of a set screw in the sleeve; the movable unit may then be guided so that the pen will draw the desired contour.

Protection for the inked lines and labels is given by a final coat of varnish; the variety known as "White Damar" varnish appears to be the most satisfactory for perfect transparency. Figure 2 shows a completed model of the system albite-anorthite-diopside.

AURICHALCITE IN MISSOURI

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The occurrence of aurichalcite, $2(\text{Zn,Cu})\text{CO}_3 \cdot 3(\text{Zn,Cu})(\text{OH})_2$, in Missouri is unreported hitherto, so far as the writer knows, and a note concerning a recent find may be in order for the record. One of the writer's students, Mr. Carl E. Paden, collected specimens in November, 1939, from the Shinn mine in Stark City, Newton County, Missouri, (near the Joplin area), which contain aurichalcite and associated sphalerite, hemimorphite, covellite, malachite, and dolomite. The ore minerals cover and cement a chert and dolomitic limestone breccia which is also cemented by secondary crystalline dolomite showing the curved crystals and pink color typical of that mineral from the Joplin region.

The sphalerite is resinous and dark brown, and highly shattered in most parts. After fracturing, solutions permeated the formation and re-

placed the sphalerite with covellite in thin layers. The covellite is very dark to black, iridescent in places, and sometimes powdery. Since oxidation is also shown on the specimens the possibility of the black powder being tenorite must not be overlooked. Tests made on the finest scrapings gave positive sulphur reactions, indicating a sulphide, but it is still possible that a little unreplaced sphalerite contributed the sulphur. However, the iridescent appearance and the fact that similar material from the same region was determined as covellite by Siebenthal¹ (1916) support the belief that all of this black material is covellite.

Oxidation, carbonation, and hydration followed the sulphide deposition. The limestone fragments show solution, iron compounds have been oxidized to brown staining limonite, and some clay is present. Sphalerite is covered along open cracks with thin hemimorphite which may also be present cementing the fragments.

The aurichalcite, an oxidation product of the copper and zinc minerals, occurs in fine, pale greenish-blue blades which radiate in bunches up to 3 or 4 millimeters in diameter. Aurichalcite has formed on top of the hemimorphite, or is mixed with the hemimorphite, where it serves as a cement, but most commonly it has replaced dolomite. The aurichalcite is not abundant as far as quantity goes, but is well developed in the small specimens at hand. Malachite is present at times as small hemispheres of radiating crystals on the hemimorphite.

Apparently after brecciation of the cherty limestone the dolomite and sphalerite were deposited between the rock fragments and replacement of sphalerite by covellite followed. Oxidation later developed hemimorphite, malachite, and aurichalcite which overlies the hemimorphite and replaces dolomite.

¹ Siebenthal, C. E., Origin of the zinc and lead deposits of the Joplin region: *U. S. Geol. Survey, Bull.* **606**, 258 (1916).

Important studies of the alkali xanthates, foremost reagents in the flotation process for metal ores, are being conducted at the Massachusetts Institute of Technology under the newly created Dow Fellowship.

The project is being started by Kenneth C. Vincent, first holder of the fellowship, and will be continued by him for a year under the direction of Professor Antoine M. Gaudin, known internationally for his outstanding work in ore dressing and recently appointed Richards Professor of Mineral Dressing at the Massachusetts Institute of Technology. A grant from the Dow Chemical Company makes the research possible.

Vincent is a graduate in chemical engineering of the University of Utah, and also holds a degree of master of science in mineral dressing from the Montana School of Mines. At the time of his appointment to the fellowship, he was research engineer for the American Smelting Company in Utah.

PROCEEDINGS OF SOCIETIES

NEW YORK MINERALOGICAL CLUB, INC.

American Museum of Natural History, New York City, January 17, 1940.

The meeting was called to order with 45 members present. The speaker of the evening was Edward Henderson of the United States National Museum, who addressed the Club upon "Meteorites and Meteorite Problems." He told the members about the collection at the National Museum, which has 53% of the 1340 known falls represented in specimens over 5 gm. in weight. He discussed the relationship of the Ni content to the pattern of the siderites and told of the work being done to learn more of the cause of the Widmanstätten patterns. He also recounted some interesting observations made in connection with recent falls and startling calculations of the size of the original mass. In addition to recording new finds, some of the research leads to grouping of meteorites originally considered as separate falls, as in the case of nine Chilean hexahedrites.

Mr. Henderson called attention to the interesting compositions of the olivines of meteorites; though intimately associated with iron, they are always nearly pure magnesium olivines. The same is true of the enstatite. Chondrules and brecciated structures also still require an explanation.

F. H. POUGH, *Secretary*

American Museum of Natural History, New York City, February 21, 1940.

The meeting was called to order with 70 members and guests present. Mr. Northup proposed the Easton quarry as the site for the Spring Excursion.

Following a brief business meeting, Mr. James L. Head of the Chile Exploration Company addressed the Club upon the "History and Development of Copper Mining at Chuquicamata, Chile." Mr. Head is well qualified to speak upon this subject as he has been intimately associated with the development of the mine during the last 16 years. Some porphyry mines may produce more tons of ore per day, but Chuquicamata is at present the greatest copper deposit on earth. It contains a billion tons of ore and over 40 billion pounds of copper. The deposit is 1.85 miles long with a maximum width of 3300 feet.

Chuquicamata is an old mine and even its name is of uncertain origin. A few Indians living on a nearby river made use of the turquoise and other colored pebbles for jewelry, but probably did not work the copper. The Spaniards undoubtedly mined the copper. Subsequently, intermittent operations exploited the higher grade ore until 1912 when A. C. Burrage of Boston and the Guggenheims started its modern development as the Chile Exploration Company. In 1923 control of the company was purchased by the Anaconda Copper Mining Co. As much as 59,000 tons of ore averaging about 1.63% Cu and 33,500 tons of waste have been removed in a single day.

Chuquicamata lies on a lesser chain of mountains to the west of the main Andean chain. The region has a complex geological history of intrusions and uplifts, with shattering and repeated mineralization. In the crushed zone many fractures developed in which the primary copper ores were deposited. The oxidized ore is not disseminated as in porphyry copper, but concentrated in innumerable fissures into which it spread after rising through the major fracture zone. The fissures vary from paper thickness to $\frac{3}{4}$ or 1 inch. The primary sulphides were probably pyrite, enargite, and covellite, together with minor amounts of chalcopyrite, tetrahedrite, bornite, and sphalerite. Uplift and arid climate has resulted in enrichment through oxidation and the formation of many rare and unusual copper and iron minerals. 95% of the ore is antlerite. Chalcantite, natrochalcite, kröhnkite, etc., are other important copper minerals.

Experiments at the Geophysical Laboratory have shown the importance of SO_2 in the oxidizing solutions as the controlling factor in determining which minerals will form. Chalcantite forms from solutions of high acidity; antlerite is characteristic of moderate acidity, brochantite of low, and CuO of very low. In arid climates, solutions are normally of higher acidity than those of humid climates, which explains the formation of the particular minerals at Chuquicamata. There are some high sulphide peaks where silica halos have protected them against oxidation. If these peaks eventually oxidize close to the surface, kröhnkite and natrochalcite, as well as chalcantite, will form as they are characteristic of high acidity. But in a feldspathic rock, with alkalis available, the acidity will rapidly diminish with depth, and antlerite soon replaces the other minerals.

Iron minerals have complicated the picture. Iron must be combined as limonite or jarosite before the copper minerals are free to separate out. Consequently, the copper minerals in solution have spread out before precipitation from the original place into post-mineral fractures. Such knowledge has turned out to be of great help in mining operations, as indicator minerals have now been determined. Much of this work has been done by O. W. Jarrel and is still unpublished.

The talk was illustrated by specimens and moving pictures, one reel of which was in color and very impressive.

F. H. POUGH, *Secretary*

MINERALOGICAL SOCIETY: LONDON

General Meeting held in the apartments of the Geological Society of London on March 7th, 1940. Mr. Arthur Russell, M.B.E., President, in the Chair.

The following papers were read:—

(1) *Mineral localities on the Mendip Hills, Somerset*. By Mr. ARTHUR W. G. KINGSBURY.

A systematic examination of this district, over several years, has led to the discovery of a number of interesting minerals not previously recorded, and to the re-discovery and collection of further specimens of other rare species already noted in small quantities.

This paper describes a large number of the localities examined, and gives the general occurrences of minerals in the area.

(2) *Colloidal gold as a colouring principle in minerals*. By Dr. J. NEWTON FRIEND and Mr. J. P. ALLCHIN.

Various factors to which minerals owe their colours are discussed. It is shown that traces of gold are present in many minerals, notably in coloured celestines and rock salts. It is suggested that the colours of these two minerals may be due to their gold contents, the gold being present in the colloid state. No gold was detected in a ruby. Sufficient amount was present in Cropwell Bishop anhydrite to account for its blue cast. A specimen of pale bluish-green aragonite from Lunehead mine, Yorkshire, is identified as the variety mosottite. Its colour is due to copper.

(3) *The composite dike at Brockhill, Worcestershire*. By Dr. J. H. TAYLOR (communicated by Dr. JAMES PHEMISTER).

The paper describes a small composite dike consisting of teschenite with thin quartz-dolerite margins intruded into the Downtonian in the valley of the River Teme in Worcestershire. The nature of the igneous and metamorphic rock types and their relations to one another are discussed, and the suggestion put forward that the quartz-dolerite has resulted from reaction between teschenitic magma and sediment.

(4) *Note on an occurrence of bertrandite and beryl at the South Crofty mine, Cornwall.* By DR. JAMES PHEMISTER.

A new locality for bertrandite and beryl in Cornwall is recorded. The minerals occur in a stanniferous veinstone and are recognizable only under the microscope. Aggregates of chlorite and bertrandite are associated with tourmaline peach and also form pseudomorphs after beryl. Beryl of a new generation occurs as prisms, needles and skeletal crystals in quartz.

(5) *Iron-rich kornerupine from Port Shepstone, Natal.* By Mr. J. E. de VILLIERS (communicated by the General Secretary).

Kornerupine, which differs from previously described material chiefly in having a higher ferric iron and lower magnesia content, is found in the Port Shepstone district, Union of South Africa. An analysis of this material shows that the composition of kornerupine varies between wider limits than hitherto known. The general formula $(R_3'', R_2''', R_6)_3(Si_3, B_4)O_{15}$ is deduced from the available analyses.

(6) *On maucherite (nickel-speiss, placodine, temiskamite).* By Dr. M. A. PEACOCK.

Chemical analyses and x-ray data for maucherite from Sudbury, Ontario, and Eisleben, Thuringia, are given. The mineral is tetragonal, a 6.84, c 21.83 Å, space-group D_4^4 or D_4^8 , and the unit cell contains $Ni_{44}As_{32}$. Walker's temiskamite is identical with maucherite.

BOOK REVIEW

MINERALOGIE IN SACHSEN VON AGRICOLA BIS WERNER. Die Ältere Geschichte des Staatlichen Museums für Mineralogie und Geologie zu Dresden (1560–1820), by WALTHER FISCHER. 356 pp., 24 pl., 18 text figures. C. Heinrich, *Dresden*.

During the 15th Century and later the Erzgebirge of Saxony was a rich and important mining area, yielding a wide variety of ores. Annaberg, Schneeberg, Freiberg, Altenberg, Johanngeorgenstadt and Zinnwald are among the most famous mineral localities known to all mineralogists. It is, therefore, natural that the interest in mineralogy should begin here early and that many important contributions to knowledge should stem from this region.

From Georg Agricola (1494–1555) through Werner (1750–1817) the story of Saxon mineralogy is followed in terms of the development of the Dresden collection, from the Kunstkammer of the Kurfürst August begun in 1560 to the modern scientific "Museum für Mineralogie und Geologie zu Dresden." Dr. Fischer, curator of the mineralogical and geological collections in the famous Zwinger, offers us, in this book, much more than an account of his institution, but a detailed chapter in the early history of our science, an account that all mineralogists can read with great interest. "Die Wissenschaft ist international, die Mineralogie aber ist sächsisch."

One half of the book (185 pp.) is given over to this historical development; the second half (115 pp.) is devoted to a series of notes, supplementing the text, devoted to collateral themes, with numerous references to old and difficultly accessible literature. A special item of interest of two pages quotes Neickelius' "Rules for Museum Visitors" of 1727, a series of 25 recommendations to help a visitor gain most from his visit.

This scholarly work has the imprint of much bibliographical research in old documents and early printed works, and should prove a valuable source book for the history of our science. It is, as well, an absorbing dissertation on mineralogical development and museum practice for casual reading.

W. F. FOSHAG

NEW MINERAL NAMES

Tirodite

J. A. DUNN, and P. C. ROY: Tirodite, a manganese amphibole from Tirodi, Central Provinces. *Rec. Geol. Surv. India*, **73**, pt. 2, 295-8 (1938), 1 figure.

NAME: From the locality Tirodi, Central Provinces, India.

CHEMICAL PROPERTIES: A silicate of magnesium and manganese of the amphibole group. Analysis: SiO_2 53.26, Al_2O_3 1.25, Fe_2O_3 2.63, FeO 1.06, MnO 8.25, MgO 31.26, CaO 1.11, K_2O 0.07, Na_2O 1.56, H_2O 0.05; sum 100.50.

PHYSICAL AND OPTICAL PROPERTIES: Color yellow. Luster vitreous. $G = 3.312$. $H = 6.5$. Cleavage prismatic, $124^\circ 20'$.

Biaxial, $2V = 88^\circ$. Optic plane (010). $Z \wedge c = 21^\circ$. Dispersion $r > v$. α (pale yellow to colorless) = 1.629, β (pale yellow) = 1.639, γ (pale yellow to straw yellow) = 1.650.

OCCURRENCE: Found as coarse bladed prisms in coarse braunite-rock and braunite-spessartite-rhodonite-quartz rock. It is of metamorphic origin.

W. F. FOSHAG

Chkalovite

V. I. GERASIMOVSKY: Chkalovite. *Compt. Rend. (Doklady) Acad. Sci. U.R.S.S.*, **22**, 259-263 (1939), 2 figures.

NAME: In honor of Valery Pavlovich Chkalov, aviator, first to accomplish the non-stop flight from Moscow, via North Pole, to United States.

CHEMICAL PROPERTIES: A sodium beryllium silicate, $\text{Na}_2\text{Be}(\text{SiO}_3)_2$. Analysis (by Pereverzeva) SiO_2 56.81, Fe_2O_3 0.30, FeO 0.12, BeO 12.67, CaO 0.37, Na_2O 28.93, K_2O 0.13, H_2O — 110° 0.23, SO_3 0.22; sum 99.78. Easily soluble in hydrochloric and nitric acids, difficultly soluble in sulfuric acid. B. B. fuses to transparent colorless glass.

CRYSTALLOGRAPHIC PROPERTIES: Orthorhombic (from Lauegram normal to good cleavage).

PHYSICAL AND OPTICAL PROPERTIES: Color white, luster vitreous. Semitransparent. Cleavage fair. Fracture uneven to conchoidal. $H = 6$. $G = 2.662$.

Biaxial, positive. $2V = 78^\circ$, $\alpha = 1.544$, $\gamma = 1.549$.

Optic axial plane parallel to the pronounced cleavage. Also shows two indistinct cleavage directions.

OCCURRENCE: Found in ussingite veinlets, somewhat resembling natrolite, in the Lovozero alkaline massifs at Punkaruaiv Mountain, Kola. Associated minerals are schizolite, sphalerite, microcline, sodalite, eudialyte, neptunite, etc.

W. F. F.

Mineral Day at the World's Fair

Monday, June 17, 1940, has been set aside as Mineral Day at the New York World's Fair. Special programs are being arranged and unusual privileges will be accorded to all interested in the mineral exhibits at the Fair.

The Society regrets to announce the death of Professor Waldemar C. Brögger, one of the eight Correspondents of the Mineralogical Society of America. Dr. Brögger passed away on February 17 at the age of eighty-eight years.